LIST OF THE OFFICERS

OF

The Institution of Petroleum Technologists, 1933-1934

Past-Presidents:

*Sir Boverton Redwood, Bart., D.Sc., F.R.S.E. (1914-1916).
Prof. Sir John Cadman, G.C.M.G., D.Sc., M.Inst.C.E., M.Inst.M.M. (1916-
The Rt. Hon. Lord Greenway of Stanbridge Earls (1917-1919). [1917)
*Sir Frederick W. Black, K.C.B., B.A. (Lond.) (1919-1921).
Prof. John Samuel Strafford Brame, C.B.E., F.I.C., F.C.S. (1921-1923).
*Herbert Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng. (1923-1925).
Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (1925-1927).
Alfred C. Adams (1927-1929).
A. E. Dunstan, D.Sc., F.I.C., F.C.S. (1929-1931).
James Kewley, M.A., F.I.C., F.C.S. (1931-1933).

President:

T. Dewhurst, A.R.C.Sc., F.G.S.

Vice-Presidents:

Ashley Carter, A.M.I.Mech.E.
C. Dalley, M.I.E.E.
Alexander Duckham, F.C.S.
Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E.
J. McConnell Sanders, F.I.C., F.C.S.
F. B. Thole, D.Sc., F.I.C., F.C.S.

Members of Council:

Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.
Sir John T. Cargill, Bart., Hon. LL.D.
A. E. Chambers, A.M.Inst.C.E.
C. H. Coxon.
A. Frank Dabell, M.I.Mech.E.
B. J. Ellis.
Elliott A. Evans, F.C.S.
F. H. Garner, Ph.D., M.Sc., F.I.C.
T. R. H. Garrett, M.A., F.G.S.
John Gillespie, M.I.Mech.E.
Prof. V. C. Illing.
J. S. Jackson, B.Sc., A.I.C.
Prof. A. W. Nash, M.Sc., F.C.S., M.I.Mech.E.
James Romanes, F.G.S.
A. Beeby Thompson, O.B.E., M.I.Mech.E., M.Inst.M.M., F.G.S.
A. Wade, D.Sc., A.R.C.S., F.G.S., M.Inst.M.M., F.Am.G.S.

Honorary Treasurer: Lord Plender of Sundridge, G.B.E.
Solicitors: Messrs. Ashurst, Morris, Crisp & Co.
Auditors: Messrs. Price Waterhouse & Co.

* Deceased.

Bankers:
WESTMINSTER BANK, LIMITED.
21, Lombard Street, London, E.C. 3.

Hon. Editor:
A. E. DUNSTAN, D.Sc., F.I.C., F.C.S.

Hon. Librarian:
A. WADE, D.Sc., A.R.C.S., F.G.S., M.Inst.M.M., F.Am.G.S.

Associate Editor, Librarian and Secretary, Standardization Committee:
GEORGE SELL.

Hon. Secretary:
ARTHUR W. EASTLAKE, M.I.Min.E., A.M.I.Mech.E.

Secretary:
Commander R. E. STOKES-REES, R.N.

Offices—Aldine House, Bedford Street, Strand, London, W.C.2.
Telegrams Instpetech, Lesquare, London.
Telephone: Temple Bar 1842.

CONTENTS.

	PAGE
Council Officers	i–ii
General Notices	v–vi
Personal Notes and Special Notices	vii–x
Reports on the Progress of Naphthology, 1932 (*continued*):	
Natural Gas and Natural Gasoline. By Miss THELMA HOFFMAN	549
Crude Oil. By W. H. THOMAS, A.R.S.M.	554
Motor Spirits and Light Distillates. By D. A. HOWES, Ph.D., B.Sc.	557
Gasoline Engines and Knock Testing. By R. STANSFIELD, A.M.Inst.C.E.	567
Kerosine and White Spirit. By S. T. MINCHIN, B.Sc., A.I.C.	574
Lubricants and Lubrication. By A. R. BOWEN, D.Sc., Ph.D., F.I.C.	578
Gas Oil, Diesel Fuel Oil and Fuel Oil. By F. H. GARNER, Ph.D., M.Sc., F.I.C.	592
Oil Engine Development. By P. N. EVERETT, A.M.Inst.C.E.	600
Asphalts and Road Materials. By W. W. GOULSTON, B.A., B.Sc., A.I.C.	617
Special Products. By E. B. EVANS, M.Sc., A.I.C.	628
Analysis and Testing. By W. H. THOMAS, A.R.S.M.	636
Standard Methods of Testing Petroleum and Its Products. By Professor J. S. S. BRAME, C.B.E., F.I.C., F.C.S.	652
Chemistry of Petroleum. By D. A. HOWES, Ph.D., B.Sc.	655
Statistics. By GEORGE SELL	673

ABSTRACTS.

PAGE

Class 100. Geographic Occurrence 255A
„ 200. Geology and Origin 256A
„ 300. Development and Production 256A
„ 400. Transportation, Storage and Distribution 268A
„ 500. Properties and Their Determination 271A
„ 600. Refining and Refineries 281A
„ 700. Utilisation 300A

AUTHOR INDEX.

The numbers refer to the Abstract Number.

Abegg, W. A., 639
Alexandroff, P., 704
Amiot, R., 648
Anderson, J., 703
Andrews, C., 700
Andrus, O. K., 694
Armstrong, G. J., 639
Arnold, J. H., 646
Atwell, H., 703

Bahlke, W., 707
Bailey, J. R., 660
Baker, H. U., 639
Baker, R. G., 639
Baker, W. L., 617
Bat. Petr. Mij., 705
Baylis, W., 703
Behimer, O., 707
Bell, J. C., 639
Beynon, C. E., 698
Bignell, L. G. E., 615, 626
Birkhimer, E., 703
Black, J. C., 700
Boutaric, A., 648
Bowen, A. R., 644
Bradford, S. C., 628
Brewster, O. C., 707
Brooks, B. T., 640
Brown, W., 640
Browne, V., 700
Brunchli, K. W., 613
Burrell, G. A., 663
Burt, C. E., 639

Campbell, S., 706
Carey, P. C., 657
Chadburn, V. R., 693
Chahnazaroff, D., 624
Chemical Reactions, Ltd., 701
Chittick, M., 700
Clark, C. L., 634
Colas Products, Ltd., 704
Cook, J. W., 658, 674
Cook, K. H., 655
Cook, W. A., 655
Cooke, F., 718
Coubrough, G., 703, 707
Coward, H. F., 653
Crandell, J. S., 721
Crickmer, C. S., 639
Cuthill, J., 639

Deutsche Gold-u.-Silber Scheideanstalt, 706
Distillers Co., 706
Dodds, R. D., 639
Dorrer, E., 701
Dougherty, H. K., 638
Dryer, C. G., 679
D. V. M., 672

Eaun, G. M., 639
Ebaugh, F., 703
Edeleanu Ges., 707
Edgeworth-Johnstone, R., 704
Edmister, W. C., 689
Egerton, I., 717
Egloff, G., 679
Ehlers, C., 661

Faben, C. R., 707
Fisher, C. H., 720
Fletcher, H. W., 639
Foley, F. B., 695
Fortune, J. C., 639
Foster, D. H., 724
Foster, W. L., 639
Fowler, J. T., 639
Fraser, O. B. J., 690
Fusstieg, R., 681

Gage, A. G., 639
Gard, E., 704
Garfield, L. E., 639
Garlick, H. S., 723
Georgeson, E. H. M., 653
Gibson, J. G., 638
Gosline, J. E., 623
Graaff, W., 639
Greutert, J., 667
Groote, M. de, 640
Guichard, P., 700

Hagan, H. H., 642
Hagiwara, S., 714
Hamaker, R. G., 639
Hammer, O., 639
Harrington, G. G., 639
Haslam, R., 701
Hayes, E. P., 627
Henderson, L., 703
Herthel, E., 702
Hewett, C. L., 658
Hieger, I., 658, 674

Higgins, A., 703
Higgins, E. C., 682
Hild, F. W., 639
Hirsch, J. H., 688
Hirt, J., 702
Hodge, J. C., 691
Hodges, F. C., 637
Hodgson, C. C., 712
Hoepfner, W., 661
Holmes, W. C., 705
Hubbard, P., 669
Hurst, W., 612

I. G. Farbenind. A.-G., 701
Ivanyse, V., 676

James, H. J., 639
Jasper, T. M., 694
Johnson, A. M., 637
Johnson, C. M., 677
Johnston, E. C., 639

Kalichevsky, V. A., 645
Kambara, S., 664
Kato, T., 652
Kennaway, E. L., 674
Kimball, C. B., 634
Kimura, I., 713
Knox, G. S., 639
Kobuyashi, R., 687
Kuhl, J., 700

Lahee, F. H., 611
Larson, L. J., 694
Leaky, R. A., 639
Leckler, P., 704
Ledeen, H., 622
Lindsly, B. E., 629
Loomis, N., 707
Louis, M., 651
Lowry, C. D., 679
Lucke, C., 707

MacCubbin, A., 707
Mallison, H., 670
Manning, S. E., 639
Maruhn, J., 701
Matsui, M., 664
Mayneord, W. V., 674
Meinzer, G., 640
Misono, A., 687

Mitchell, W. J., 639
Miuta, M., 656
Mono Ges., 673
Moore, T. V., 612, 636
Morrell, J. C., 679, 702
Moss, R., 639
Murdock, R. A., 639

Nagle, W. M., 607
Nellensteyn, F. J., 668
Newcombe, R. B., 625
Nieuwland, J. A., 673

Oberbach, J., 719
O'Brien, M. P., 623
O'Grady, D. J., 639
Oksenholt, J. H., 639
Osborne, H., 639
Osterberg, A., 706
Ostrander, V. L., 722
Otis, H. G., 631, 639

Paynter, W., 704
Pearce, W. L., 639
Peizer, H., 700
Petty, E., 703
Pew, A., 700
Peyrot, M., 651
Pier, M., 701
Podbielniak, W. J., 650
Pöll, H., 686
Putnam, M., 614
Pyhala, E., 654

Reed, C. E., 639
Reed, D. H., 639
Reid, D. H., 639
Reid, E., 705
Reistle, C. E., 627
Ricker, N. H., 639
Rogers, W. F., 620
Roodenburg, N. M., 668
Rosenberg, I., 703
Ross, D. T., 621
Ruhrchemie A.-G., 705

Saal, R. N. J., 647
Salmony, A., 678
Sandstone, H. D., 639
Sawdon, W. A., 619
Schaeffer, J., 703
Schilthuis, R. J., 612
Schuster, M., 700
Sclater, K. C., 630
Scott, F. L., 639
Shepard, E. R., 641
Sievers, W. E., 639
Simons, J. K., 663
Smith, F. L., 717
Smith, J. C., 657
Smith, J. T., 609
Smith, O. C., 689
Snow, H., 700
Spangler, H. J., 680
Speller, F. M., 699
Stand. Oil Devel. Co., 705
Standiee, H. R., 639
Steele, S., 710, 716
Storer, G. P., 671
Story, B. W., 645
Stroud, P. W., 708
Sturgis, A. C., 685
Subkow, P., 639
Sulda, H., 688
Swindell, F., 618

Tanaka, Y., 987
Tarlton, P. E., 639
Tate, W., 701
Taylor, M., 702
Taylor, R. A., 701
Turner, N. C., 683
Tuttle, M., 703

Ubbelohde, L., 649
Uhler, A. S., 639

Vaughn, T. H., 673
Veeder, J. K., 696
Verver, C. G., 647
Vitovec, F. J., 650

Wagner, E. C., 663
Walker, J. P., 639
Waters, M. F., 639
Wayne, T., 640
Weston, P. E., 662
White, E. S., 639
Williams, W. J., 639
Wilson, C. O., 684
Wirshing, H., 709
Wright, J. C., 639

Yamada, T., 666
Yeaton, S., 700
Yonker, M., 702

Zeigler, H. B., 639

DESIGNATION OF MEMBERSHIP.

Members wishing to indicate their membership of the Institution are reminded that the correct abbreviations as laid down in the By-Laws, Section III., Paragraph 9, are: Hon.M.Inst.P.T. for Honorary Member; M.Inst.P.T. for Member; A.M.Inst.P.T. for Associate Member; Stud.Inst.P.T. for Student; and Assoc.Inst.P.T. for Associate.

The Institution has now been placed on the Loan List of the Science Library, South Kensington, and members of the Institution wishing to obtain books from the Science Library should consult the Institution's Librarian, who will make the necessary arrangements.

The attention of members is also called to the improved facilities available in the Member's Room at the Institution's offices. The number of writing tables has been increased and members will find this room a convenient place, both for consulting books and journals and for conducting their own correspondence.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

NOTICES.

The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright. Authors of papers and articles are requested to transfer their copyright to the Institution for a period of six months from the date of receipt of the paper. Such transfer should be made in writing when the manuscript is forwarded to the Editor.

Editors are permitted to publish abstracts, providing that acknowledgment is made to The Institution of Petroleum Technologists.

Issue of Journal. The Journal is issued in twelve parts per volume, commencing in January of each year.

Members whose subscription is not in arrear receive the Journal free of cost, and additional copies are charged at the rate of 7s. 6d. per part, unless otherwise stated. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

Changes of Address. Members are requested to notify any change of address to the Secretary.

Papers and Articles. Members are invited to submit papers to be read at the General Meetings of the Institution, and are specially asked to forward articles for consideration for publication in the Journal. Diagrams, illustrations, etc., should be suitable for direct photographic reproduction. Authors are informed that all papers, whether for reading or for publication, will be submitted to a referee nominated by the Publication Committee.

Authors of papers published in the Journal are entitled to receive 25 free reprints of their contribution. Further copies may be obtained on payment, and orders for these should be sent to the Secretary when the manuscript is forwarded to the Editor. The free reprints do not include any discussion which may be published with the paper, but authors may have such discussion included in their reprints on payment of the additional cost.

Galley proofs of the paper to be read at a General Meeting are available at the time of the meeting, but members desirous of receiving such galley proofs in advance should apply to the Secretary.

Binding of Journals. Members desiring to have their Journals bound in cases should send them, together with a remittance of 5s. 6d. per volume, to Messrs. Speaight & Sons, Ltd., 98, Fetter Lane, London, E.C. 4. A charge of 7s. 6d. will be made for binding Vol. 10, 1924. Remittance in all cases must accompany the order.

Abstracts. Abstracts of the more important articles and patent specifications are published with each issue of the Journal, this supplement being paged independently of the transactions. Members and Journal Subscribers desiring to have the Abstracts printed on one side of the paper only can be supplied with these at a charge of 10s. per annum per copy, payable in advance.

Medals. The Redwood Medal is awarded, at the discretion of the Council, as and when desirable, but not more than once each year, to a petroleum technologist of outstanding eminence, irrespective of nationality or membership of the Institution.

A medal and a prize of five guineas is awarded annually by the Council to that Student Member of the Institution who shall, in their opinion, have presented the best paper during the session.

Benevolent Fund. The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register. A register of members requiring appointments is kept at the office of the Institution for the convenience of firms requiring the services of petroleum technologists, etc., it being understood that the Institution accepts no responsibility and gives no guarantee.

Library. The Institution's Library may be consulted between the hours of 10 a.m. and 5.30 p.m. daily. (Saturdays, 10 a.m. to 12 noon.)

Advertisements. Advertisements are inserted in the Journal, and information as to terms, etc., can be obtained from the Advertising Manager, at the offices of the Institution, Aldine House, Bedford Street, W.C. 2. (Telephone No. Temple Bar 1842.)

Prepaid small advertisements, such as situations vacant and wanted, patents for sale and miscellaneous, are accepted at a charge of 1s. per line of seven words (minimum 4s.). Box number 1s. extra. These should be sent to the Associate Editor not later than the 12th of the month in which it is desired they should appear.

LIST OF ADVERTISERS.

Members are desired when making enquiries or placing orders with advertisers to mention that they have seen their announcement in the Journal.

W. Christie & Grey, Ltd.
A. F. Craig & Co., Ltd.
Duke & Ockenden, Ltd.
W. Edwards & Co
Foster Wheeler, Ltd.
W. J. Fraser & Co., Ltd.
Hadfields, Ltd.
John G. Stein & Co., Ltd.
Stewarts & Lloyds, Ltd.
Tintometer, Ltd.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. L. A. Bushe is home from Trinidad.
Dr. F. G. Clapp has returned to New York from Persia.
Mr. A. Frank Dabell is home from Trinidad.
Dr. L. Edeleanu has left France, and is in Rumania.
Dr. H. G. Kugler has left Trinidad, and is in Switzerland.
Mr. V. Laycock is home from Persia.
Mr. R. C. Parker has returned from Burma.
Mr. H. E. F. Pracy has left for Trinidad.
Mr. F. G. Rappoport is home from Venezuela.
Mr. T. Robathan has returned from Ecuador.
Mr. C. V. Rutherford is home from Persia.
Mr. E. Stokoe has returned from Belgium.
Mr. J. Westbury is home from Trinidad.
Mr. C. J. Wright has left Persia and is in England.

The Secretary would be glad to learn of the whereabouts of the following members: E. E. G. Agius, A. E. C. Corbet, E. J. S. Hewitt, A. MacLean, D. J. Pull, P. A. Stiff and R. W. Stiles.

STANDARD METHODS OF TESTING PETROLEUM AND ITS PRODUCTS.

SECOND EDITION.

Giving full details of revised and new Methods of Test of Petroleum and Its Products.

Price: 7s. 6d. net.

To members of the Institution, marked "Member's Copy," 5s. net.
(Limited to one copy per member.)

REPORTS ON THE PROGRESS OF NAPHTHOLOGY, 1932.

Reprinted from the June and July issues of the Journal, 1933.

Price: 10s. 6d. net.

MEASUREMENT OF OIL IN BULK.

PART I.—STANDARD WEIGHTS AND MEASURES.

Giving authoritative information regarding the fundamental units of weight and measurement in the Imperial, U.S.A., and Metric systems. with a Table of Recommended Contracted Ratios for general use in the petroleum industry.

Price: 2s. 6d. net.

All the above to be obtained from the office of the Institution.

ALDINE HOUSE, BEDFORD STREET, STRAND, LONDON, W.C. 2.

Natural Gas and Natural Gasoline.

By Miss THELMA HOFFMAN.

DURING the years 1930–31, new uses and by-products have magnified the importance of natural gas. The expansion of pipe lines and the use of liquified petroleum products have increased the use of natural gas as a domestic fuel. In spite of these advances, the production of natural gas in 1930 increased only a small amount—1·3 per cent.[1] This is in sharp contrast to the unprecedented expansion of 1929. In 1931 occurred the first decrease in production in ten years.[2] A comparison can be obtained by a consideration of the following statistics :—

Year.	Production.
1928	1,568,139,000,000 cu. ft.
1929	1,917,693,000,000 cu. ft. increase of 22%.
1930	1,943,421,000,000 cu. ft. increase of 1·3%.
1931	1,686,436,000,000 cu. ft. decrease of 13%.

This decrease in production of natural gas has been attributed to the following factors : first, that less field work has been done ; second, that refineries are now using gas from the cracking processes as fuel rather than natural gas and finally, that carbon black production has decreased. The consumption of natural gas for domestic and industrial heating increased 1·2 per cent. in 1931. This is due to the increase in the area served following completion of several new pipe lines. In 1931, California replaced Oklahoma as second in gas production. Texas continues to rank first.

The average price of natural gas for domestic use has shown a steady increase, being 62c. per 1000 cu. ft. in 1929, 63½c. per 1000 cu. ft. in 1930 and 65½c. per 1000 cu. ft. in 1931.

PIPE LINES.

In the Annual Pipe Line Number of the *Oil & Gas Journal* (June 4, 1931), maps are given of the many new areas now being served. The location of a route for a new pipe line has always been a problem of great importance. Now, the engineer has new data to assist him in locating the best and shortest route—the aerial survey.[3] The Southern Union Gas Company used this method in locating their new line in New Mexico. In addition to locating the route, aerial survey stakes were dropped from an airplane flying low.[4]

One of the more important improvements in welding pipe is the use of the shielded electric arc.[5] This method produces a

[1] " Natural Gas in 1930, *U.S. Mineral Resources*, 1930.
[2] " Production of Natural Gas in 1931," *U.S. Bur. Mines, Mineral Market Report M.M.S.*, 151.
[3] H. Nelson, *Oil & Gas J.*, 4.6.31, **30** (3), T120.
[4] W. Reid, *Oil & Gas J.*, 4.6.31, **30** (3), T66.
[5] C. M. Taylor, *Oil & Gas J.*, 4.6.31, **10** (3), T115.

weld resistant to corrosion, ductile as the pipe and with a high tensile strength. Corrosion of the pipe is a source of a great deal of trouble and expense. The Bureau of Standards has been conducting some important research work on the corrosivity of soils and the method of conducting soil tests.[6] Definite knowledge of the effect of the soil in the route chosen would be of the greatest value in determining the correct type of pipe protection.

Odorization.

With the general introduction of natural gas for domestic heating, the problem of detecting small leaks became very important. The evil smell of manufactured and mixed gas was usually sufficient warning, but as natural gas is practically odourless, it is necessary to add a warning agent. The selection of a proper odorant has been given a great deal of attention during the years 1930–31.[7,8] Ethyl mercaptan,[9] and Calodorant No. 3,[10] an odorant developed by the Standard Oil Company of California, have been the most commonly used. The choice of an odorant depends on many factors. Among these are the corrosive nature of the warning agent, toxicity, effectiveness and cost. It has been necessary to develop special equipment to inject this material into the gas lines.[10,11]

Natural Gasoline.

Even though the greatest volume of natural gas consumed has been in field operations, industrial and domestic heating, natural gasoline and its by-products, butane and propane, are very important products of natural gas. Natural gasoline plants used $6\frac{4}{10}$ per cent. more natural gas in 1930 than in 1929, but the yield of gasoline was 1 per cent. less.

Production of natural gasoline in 1930 2,210,000,000 gals.
" " " 1931 1,800,000,000 gals. (est.)[12]

This decrease in yield is due to the installation of new plants designed to treat large quantities of gas, but without the recovery of all the gasoline available. The second factor in this decrease of yield is a demand for a " stabilised " gasoline for blending.

Butane and Propane—Liquefied Petroleum Gases.

The desire for a more stable gasoline, by the removal of the more volatile fractions, gives rise to the two valuable by-products

[6] E. R. Shepard, *Oil & Gas J.*, 4.6.31, **10** (3), T40.
[7] *U.S. Bureau of Mines*, Tech. Paper 480.
[8] *Western Gas*, **6**, 111–114.
[9] R. R. Sayers, A. C. Fieldner, W. P. Yant, R. D. Leitch and S. J. Pearce, *U.S. Bur. Mines Reprts. Invest.*, 3007, 1930.
[10] R. L. Hamilton and J. T. Rutherford, *Oil & Gas J.*, 4.6.31, **30** (3), T125; *J. Inst. Petr. Techn.*, 1931, **17**, 394A.
[11] *Gas Age Record*, **66**, 859–64.
[12] *J. of Land and Public Utility Econ.*, **8**, 309.

of the natural gasoline industry—butane and propane. Butane has been found to be a most satisfactory gas for industrial heating. As a fuel it is very clean and allows an easy control of temperature. For these reasons, many new uses are being found for it, such as in oxy-butane cutting torches, in heat treating of metals and in the ceramic and glass industries.[13] Gas from butane-air plants is successfully replacing manufactured gas in many small communities. There have been many descriptions of this type of installation.[14,15] Butane is used with manufactured gas to enrich water gas, blue gas, or other gases of low thermal value. At times it is used with manufactured gas in meeting peak-load conditions.[16]

The "bottle gases" (liquefied petroleum gas distributed in steel cylinders), are largely propane. The development of this form of fuel for domestic use has brought gas into many rural and mountain areas which could not be served by any other means, and the use of this fuel is increasing rapidly. Its only real competitor is electricity. The number of "bottle gas" retail customers was 55,000 in 1929, 117,000 in 1930 and 150,000 in 1931.

The use of liquefied petroleum gas as both a fuel and a refrigerant for a truck, is an interesting development of the Shell Oil Company of California. This truck allows the liquefied gas to expand, thereby cooling the refrigerating section of the truck. The gases are then burned as fuel.[17]

Chemical Products.

The gaseous paraffin hydrocarbons as found in natural gas are recognised as raw material for many valuable organic substances. Liquid fuels, solvents and synthetic resins may have natural gas as their starting point. A symposium on "Utilisation of Gaseous Hydrocarbons" was presented before the American Chemical Society at their meeting in Buffalo in September, 1931.[18] The three main types of chemical treatment giving rise to different products are: pyrolysis, oxidation and chlorination.

1. *Pyrolysis.*—One of the most important developments in this line is the reforming of natural gas.[19,20] This treatment produces a gas composed of methane and hydrogen rather than the original mixture of methane and higher paraffins. An increased use for hydrogen is found in the hydrogenation of petroleum and vegetable oils and it is probable that this process will be used more in the

[13] *Chem. Markets*, **31**, 43.
[14] *Ind. Eng. Chem.*, **23**, 1190–96.
[15] *Western Gas*, **7**, 28–30, 53–54.
[16] *J. West. Soc. Eng.*, **34**, 448.
[17] *Nat. Petr. News*, 2.12.31, **23** (48), 33–34.
[18] *Ind. Eng. Chem.*, 1932, **24**, 10–27.
[19] U.S. Bureau of Mines Tech. Paper 483.
[20] W. W. Odell, U.S. Bur. Mines Repts. Invest. 2991, 1930.

future. The Shell Chemical Company of California uses natural gas from the Kettleman Hills in its Reforming plant as a source of the hydrogen used in the production of ammonia.[21]

The pyrolysis of methane yields higher hydrocarbons,ethylene, acetylene, benzene, naphthalene, anthracene and pyrene. The unsaturated compounds formed by this heat treatment are subject to polymerisation. The liquids similar to benzene are believed by some to be a future source of motor fuels. Solids resembling resins and tar may be used in the future as a source of resins for paints, varnishes and plastics. Some of the ingredients of the tar may prove of interest as sources of raw material for dye-stuffs. The yield of these products depends on the temperature and rate of flow of the gas.[22]

Carbon Black.—Although the manufacture of carbon black has dropped off in 1931, due to over production and decrease in price, it is still an important product. More natural gas is used for the production of carbon black than for any other use, except fuel. Carbon is a by-product in all types of natural gas pyrolysis, however, in the Thermatomic Process for cracking methane, carbon black is the principal product.[23] The Flame Pressure process for producing carbon black depends on the control of combustion by an increased pressure.[24]

2. *Oxidation*.—In spite of the large amount of research being done on oxidation of natural gas hydrocarbons, there has been only a small amount of commercial operation. A cyclic process has been developed at the U.S. Bureau of Mines for converting natural gas or other gases rich in methane, into carbon monoxide and hydrogen by either of two reactions :—

$$CH_4 + H_2O = CO + 3H_2$$
$$CH_4 + CO_2 = CO + 2H_2$$

In this process, the gases are passed over a catalyst bed, heated to temperatures between 900–1100° C.[25] This mixture of gases may be used to produce methanol. By means of other catalysts and oxidising agents, such organic compounds as acetone and formaldehyde have been produced.[26] A process for oxidation of natural gas to formaldehyde by means of nitrogen oxides has been developed. By re-cycling, the yield of formaldehyde is increased

[21] L. Rosenstein, *World Petr.*, 1932, **3**, 31–33.
[22] U.S. Bureau of Mines Repts. Invest. 3143 ; *Nat. Petr. News*, **23** (43), 69–86.
[23] R. L. Moore, *Ind. Eng. Chem.*, 1932, **24**, 21–23.
[24] A. W. Francis, *Ind. Eng. Chem.*, 1931, **23**, 612–617 ; *J. Inst. Petr. Techn.*, 1931, **17**, 435A.
[25] C. O. Hawk, P. L. Golden, H. H. Storch and A. C. Fieldner, *Ind. Eng. Chem.*, 1932, **24**, 23–27.
[26] H. M. Smith, U.S. Bur. Min. Int. Circ. 6388, 1930.

appreciably.[27] Complete oxidation of natural gas would, of course, yield carbon dioxide. A plant has been erected in Tulsa, Oklahoma, using this source of carbon dioxide in the manufacture of "dry ice."[28]

3. *Chlorination.*—By chlorination of natural gas, such products as methyl chloride, chloroform and carbon tetrachloride should be available. So far, success seems to be limited to laboratory scale operations. These products are valuable as intermediates in building up alcohols and other organic compounds. Extensive experimental work is being done on this type of chlorination, as a result of the low cost of chlorine and natural gas.[29]

The higher hydrocarbons are more easily chlorinated, and the Sharpless Solvent Co. have produced high boiling solvents by the chlorination of pentanes obtained from natural gas.[30]

Other Uses.—Natural gas has been used in the bright annealing of metals. It has been found that these hydrocarbon gases are more suitable than pure hydrogen for checking oxidation during the annealing process.[31] It is probable that many metallurgical plants will at some future time, utilise natural gas in reducing ores to metals. At the present time, this work is in the experimental stage.[32]

Conservation.

Definite progress has been made to prevent the enormous loss of natural gas. The voluntary curtailment of the oil industry in 1931, aided the State and Federal regulation. The Federal Oil Conservation Board has suggested that a general survey be made to determine the source and amount of wastage. The total annual loss of natural gas has never been compiled, but estimates have been given for some areas. (The magnitude of this loss becomes more apparent upon a consideration of some of this data.) The Federal Oil Conservation Board Report for 1930 estimated the daily loss from Kettleman Hills alone to be more than 300,000,000 cu. ft. This amount was reduced about 70 per cent. in 1931, the daily wastage being 107,000,000 cu. ft. The Corporation Commission of Oklahoma estimated the average daily loss for 1930-31 for the Oklahoma City field to be 300,000,000 cu. ft. Great losses of gas occur in Texas. Evidence shows that this waste will be materially reduced in 1932.[33]

---

[27] C. H. Bibb, *Ind. Eng. Chem.*, 1932, **24**, 10–12.
[28] *Nat. Petr. News*, 5.8.31, **23** (31), 45.
[29] *Ind. Eng. Chem.*, 1932, **24**, 15–16.
[30] L. H. Clark, *Ind. Eng. Chem.*, 1930, **22**, 439–443.
[31] E. G. de Coriolis and R. J. Cowan, *Ind. Eng. Chem.*, 1932, **24**, 18–20.
[32] Methane as Metallurgical Reagent, C. G. Maier, A.C.S. Petr. Div. Preprint, Buffalo, 1931.
[33] *Oil & Gas. J.*, 17.11.32, **31** (26), 136.

Crude Oil.

By W. H. Thomas, A.R.S.M. (Member).

The examination of certain American crude oils has formed the subject of quite a number of publications, the oils from the East Texas field perhaps receiving the greatest amount of attention. Crudes from various sections of the field have been examined[1,2] and shown to be of mixed-base type, low sulphur content and high motor spirit yield. A similar oil is that of the Greasewood Flat area of Colorado[3], which, however, appears to contain a high wax content and is a good base for the manufacture of cylinder stocks Referring again to Texas,[1] it has been shown that the crude from the Van Field of East Central Texas has a higher gravity and sulphur content than the East Texas oil, but is of paraffin base, and, moreover, only contains two-thirds of the motor spirit fraction. According to a recent analysis the crude oil from the New Conroe field (Texas Gulf Coast area)[4] contains high proportions of gasoline and kerosine, while additional wells have indicated a large potential supply.

Garton[5], in his review of the crude oils of Oklahoma City field, has given detailed analyses of 21 samples, which were of paraffin or intermediate base, the former type predominating. The oils are generally of low sulphur content and contain about 30 per cent. of motor spirit fraction, while pour points vary between —5° and 30° F. Another investigation of Oklahoma crude is that dealing with the cracking of the Garber oil.[6] Topped crude (42 per cent. residue) is used as cracking stock in a combination liquid-vapour-phase cracking plant, while the heavy naphtha and kerosine are passed to a reforming unit, the two cracked distillates being bulked for treatment and redistillation. Commercial production of crude oil from Rankin County, Mississippi, has been obtained during 1932,[7] the oil being of heavy asphaltic base and free from paraffin. It yields 30 per cent. of gas oil, 25 per cent. of lubricating oil distillate and 43 per cent. of asphalt. Nelson and Egloff[8] have given

---

[1] Garton, *U.S. Bur. Mines Repts. Invest.*, 3130, 1931 ; *J. Inst. Petr. Techn.*, 1931, **17**, 500A.

[2] Trusty, *Refiner*, 1932, **11**, 48 ; *J. Inst. Petr. Techn.*, 1932, **18**, 119A.

[3] Rue, *U.S. Bur. Mines Repts. Invest.*, 3174, 1932 ; *J. Inst. Petr. Techn.*, 1932, **18**, 297A.

[4] *Oil & Gas J.*, 16.6.32, **31** (4), 34 ; *J. Inst. Petr. Techn.*, 1932, **18**, 298A.

[5] Garton, *U.S. Bur. Mines Repts. Invest.*, 3180, 1932 ; *J. Inst. Petr. Techn.*, 1933, **19**, 41A.

[6] Ziegenhaim, *Oil & Gas J.*, 11.8.32, **31** (12), 9 ; *J. Inst. Petr. Techn.*, 1932, **18**, 377A.

[7] *Oil & Gas J.*, 25.8.32, **31** (14), 14 ; *J. Inst. Petr. Techn.*, 1932, **18**, 377A.

[8] Nelson and Egloff, *Oil & Gas J.*, 20.10.32, **31** (22), 42 ; *J. Inst. Petr. Techn.*, 1932, **18**, 461A.

a description of the crude from Lost Soldier field of Wyoming, together with details of the yields of cracked products using a flash method of continuous operation. The same authors[9] have published the yields and analyses of products obtained from Santa Fé Springs field by distillation and by cracking, and in yet another publication[10] full descriptions have been given of the two types of crude produced from the Kettleman Hills field. One of these contains as much as 86–90 per cent. of straight-run motor spirit, and the other 37–46 per cent., the latter yielding 74·3 per cent. of motor fuel on cracking. The cracking of the residue obtained after the removal of motor spirit yielded, under the same conditions, 58·6 per cent., or 36·4 per cent. on crude base. It was noted that a higher yield of superior anti-knock value, but similar end-point, was obtained by the direct cracking of the crude.

Turning now to South America, attention should be drawn to an interesting paper[11] on the properties of Peruvian crudes, the production of which began before 1896. The similarity of the oils from the Lobitos, Restin, Lagunitas and Negritos fields is indicated, and it is stated that, in comparison, the oils from La Brea and La Breita are heavier and contain less motor fuel; sulphur contents, however, in all cases are low. Oil has been found in southern Peru, but production is not of industrial importance. A similar publication[12] has dealt with the properties and cracking yields of Argentine crude from the Comodoro, Plaza Huincul, Mendoza and Salta-Jujuy fields. The first and last of these yield asphaltic oils of similar character and low motor fuel content, the Plaza Huincul oil is much lighter, giving a high yield of motor fuel, while Mendoza oil is "intermediate" in type.

The oil from Patagonia[13] is worthy of comment in that it combines a high gravity with an unusually high percentage (25 per cent.) of water in a dispersed state. Coalescence of this water is effected by a high potential electrical current.

In view of previous unsuccessful efforts to obtain free oil from Alberta tar sands or to use its bitumen content for road purposes or as a normal crude for treatment or cracking, Boomer and Warren[14] have studied the possibility of hydrogenating the

[9] Egloff and Nelson, *Oil & Gas J.*, 14.1.32, **30** (35), 18; *J. Inst. Petr. Techn.*, 1932, **18**, 80A.

[10] Egloff and Nelson, *Oil & Gas J.*, 31.3.32, **30** (46), 75; *J. Inst. Petr. Techn.*, 1932, **18**, 207A.

[11] Egloff, Nelson and Truesdell, *Oil & Gas J.*, 1931, **30** (20), 22; *J. Inst. Petr. Techn.*, 1931, **17**, 500A.

[12] Nelson and Egloff, *Oil & Gas J.*, 1931, **30** (23), 22; *J. Inst. Petr. Techn.*, 1931, **17**, 538A.

[13] Dennis, *Ind. Chem.*, 1932, **8**, 281; *J. Inst. Petr. Techn.*, 1933, **19**, 2A.

[14] Lauriston, *Oil & Gas J.*, 8.9.32, **31** (16), 9; *J. Inst. Petr. Techn.*, 1932, **18**, 428A.

bitumen. It is concluded, however, that further work is necessary to decide whether cracking or hydrogenation is the most suitable treatment of the tar, especially as batch operation was used instead of the continuous method normally used on the large scale. Dealing with the analysis of Alberta tar sands, Clark and Pasternack[15] have described an apparatus and procedure for determining the yield of bitumen.

With regard to European crude oil, perhaps the most interesting feature is the increase of German production, due mainly to the opening up of a new field near Menteroda in Thuringa,[16] the oil having first been discovered in a potash mine 3000 ft. deep. Other German oils have been described by Nelson and Egloff,[17] namely, those of the Nienhagen and Edessa fields. The former yields an asphaltic oil of relatively high sulphur content, while the latter gives an oil containing about 25 per cent. of motor fuel and a residue suitable for cracking purposes. The main production of Czechoslovakia is a naphthenic oil from the Egbell and Hodonin fields,[18] another type being paraffinic is obtained in smaller quantites from the Bohuslavice, Turzovka and Mikovd fields.

In an article on the general properties of Japanese petroleum, Kobayashi[19] has described the analysis of the crude oils from five regions in Nishiyama (north Japan), and concluded that naphthenes and paraffins are the chief constitutents of Japanese petroleum.

[15] Clark and Pasternack, *Ind. Eng. Chem.*, 1932, **24**, 1410; *J. Inst. Petr. Techn.*, 1933, **19**, 42A.

[16] Kauenhowen, *Oil Weekly*, 1.1.32, **64** (3), 16; *J. Inst. Petr. Techn.*, 1932, **18**, 77A.

[17] Nelson and Egloff, *Oil & Gas J.*, 1931, **30** (16), 30; *J. Inst. Petr. Techn.*, 1931, **17**, 511A.

[18] Nelson and Egloff, *Oil & Gas J.*, 10.12.31, **30** (30), 22; *J. Inst. Petr. Techn.*, 1932, **18**, 45A.

[19] Kobayashi, *Petr. Z.*, 24.2.32, **28** (8), 10; *J. Inst. Petr. Techn.*, 1932, **18**, 119A.

Motor Spirits and Light Distillates.

By D. A. Howes, Ph.D., B.Sc. (Associate Member).

Introduction.

Despite the rapid growth of suitable Diesel engines for automotive purposes, gasoline is still the main product of the petroleum industry, and is likely to remain so for a long period. On the other hand, the high-speed Diesel engine is developing at a rapid rate, and this development, in England at any rate, is bound to have its effects upon gasoline sales in the near future.

Another feature of interest is the outstanding development of alcohol-gasoline blends in Europe, where numerous countries have recently imposed legislature whereby the use of alcohol as a fuel has been made compulsory. The use of compressed coal gas as a fuel is also making headway, particularly in France, but also in the United Kingdom. Such developments receive an impetus from the existing high taxes on gasoline. Liquid fuels of to-day and to-morrow is the subject of an interesting paper by Dunstan.[1]

Nomenclature.

Steps are now being taken to bring into effect a measure of real international co-operation in the subject of motor fuel nomenclature.[2] That this is a pressing need has been evident for some time.

Properties of Gasolines Produced from Various Crude Oil.

The Garber, Oklahoma 43·5–44° A.P.I. crude, when processed in pipe stills and fractionating equipment, has been reported by Ziegenhain[3] to yield 13·4 per cent. of a 150° C. end point gasoline of an octane number of 61. Crude oil from the new Conroe field, Montgomery County, Texas Gulf coast area, is typified by its high content of gasoline and kerosine (33 per cent. gasoline of 235° end point, and 17·5 per cent. of 287° end point kerosine.)[4]

Gasolines obtained by the straight running and cracking of Kettleman Hills crude oils have been described in detail by Egloff and Nelson.[5] Of these, the lighter crude, which is of about 60°

---

[1] Dunstan, *J.S.C.I.*, 1932, **51**, 822, 846; *J. Inst. Petr. Techn.*, 1932, **18**, 463A.

[2] *J. Inst. Petr. Techn.*, 1932, **18**, 874.

[3] Ziegenhain, *Oil & Gas J.*, 11.8.32, **31** (12), 9; *J. Inst. Petr. Techn.*, 1932, **18**, 377A.

[4] *Oil & Gas J.*, 11.8.32, **31** (12), 9; *J. Inst. Petr. Techn.*, 1932, **18**, 377A.

[5] Egloff and Nelson, *Oil & Gas J.*, 31.3.32, **30** (46), 75; *J. Inst. Petr. Techn.*, 1932, **18**, 207A.

[6] Nelson and Egloff, *Oil & Gas J.*, 10.12.31, **30** (30), 22; *J. Inst. Petr. Techn.*, 1932, **18**, 45A.

A.P.I. gravity (sp. gr. 0·739), contains 86–90 per cent. gasoline, while a crude from the Ochsner zone of the Temblor formation (Kettleman Hills) contains about 36–46 per cent. gasoline.

Cracked gasolines from Egbell, Czechoslovakia crude oil have been shown to have high octane numbers, 86–89, and details regarding the properties of representative Japanese gasolines have been published.[7]

PROPERTIES OF GASOLINES MARKETED IN U.S.A., 1931–1932.

In the semi-annual gasoline survey conducted by the U.S. Bureau of Mines in August, 1931[8], 319 samples from 19 areas of the United States were examined. Only two of these samples failed to pass the corrosion test. Nearly 90 per cent. of the samples contained less than 0·1 per cent. of sulphur. With regard to vapour pressures only one sample was found to exceed 10 lb., the Federal Specification limit, but in general the vapour pressures were higher than those recorded in the Survey of August, 1930. All but two of the premium priced gasolines were artificially coloured, and 26·2 per cent. of the competitive price gasolines had a colour darker than 10 Saybolt. These figures show an increasing tendency to colour gasolines artificially. Tested by the Bureau of Mines steam oven method, which indicates the amount of preformed gum present, 90·9 per cent. of the samples contained less than 5 mgms. of gum per 100 ml., nine samples were found to contain more than 10 mgms. of gum, while the highest value was 45 mgms. Octane number knock ratings were also determined on a C.F.R. engine. The average value for competitive price grades was found to be 60·8, and that of premium price grades 75·6, a slight decrease from the average results of the previous survey.

Proposed specifications for winter and summer gasolines have been approved by a committee of the Western Refineries Petroleum Association.[9]

PROPERTIES OF GASOLINES MARKETED IN THE UNITED KINGDOM.

The various gasolines, benzole mixtures and other motor fuels, sold in the English market, 1931–32, have been examined by Whatmough and reported in detail in the *Automobile Engineer*.[10]

The figures quoted show that during the past few years considerable improvement in both the knock rating and the volatility of English petrols has been made.

---

[7] Mizuta, *J.S.C.I.*, Japan, 1931, **34**, Suppl. Binding, 454, 490.

[8] *U.S. Bur. Mines Reprts. Invest.*, 3162 and 3175, 1932: *J. Inst. Petr. Techn.*, 1932, **18**, 255A, 303A.

[9] Willson, *Oil & Gas J.*, 14.4.32, **30** (48), 16; *J. Inst. Petr. Techn.*, 1932, **18**, 211A.

[10] Whatmough, *Aut. Eng.*, 1931, **21**, 229, 271, 311, 350, 384, 529, 588; 1932, **22**, 27, 75, 114, 181, 231; *J. Inst. Petr. Techn.*, 1932, **18**, 85A, 164A, 256A.

THE ANTI-KNOCK VALUES OF GASOLINES AND HYDROCARBONS.

Our knowledge of the knock ratings of pure hydrocarbons has been extended considerably during the past year, due particularly to work carried out by Garner and Evans[11] and by Garner, Wilkinson and Nash.[12]

The former investigators have dealt with naphthene and aromatic hydrocarbons and formed the following conclusions :—

1. In the cyclohexane and cyclopentane series, the octane number decreases as the number of carbon atoms in the molecule is increased.

2. In the aromatic hydrocarbon series the octane number increases until the member of the series containing nine carbon atoms is reached, and in general the octane number of aromatic hydrocarbons is less affected by substitution in so far as knock rating is concerned than other series of hydrocarbons.

3. Lovell, Campbell and Boyds' rule that the more centralised the molecule the higher the knock rating holds in the case of the cyclopentane, cyclohexane and aromatic hydrocarbons investigated.

4. The octane number at 300° F. shows lower figures than at 212° F. with the lower members of the series, but in the higher members of the series of octane number is greater at 300° F. than at 212° F.

5. In so far as the increase in octane number is concerned when lead is added to the members of the various hydrocarbon series, the increasing order of susceptibility is aromatics, cyclohexanes, cyclopentanes and, most responsive of all, α olefines.

Other workers have also examined pure hydrocarbons in this way. Hoffman and his co-workers[13] tested 30 per cent. volume mixtures of various hydrocarbons in a standard gasoline in a variable compression engine, noting the compression ratio at which knocking just ceased under full load. As a result of this work they confirmed the work of Boyd and co-workers in that :—

(*a*) Anti-knock quality in normal paraffins decreases with increasing length of chain.

(*b*) In a series of isomeric paraffins it increases with branching of the chain.

(*c*) In olefines it is greater than in the corresponding saturated hydrocarbons.

---

[11] Garner and Evans, *J. Inst. Petr. Techn.*, 1932, **18**, 751-758.

[12] Garner, Wilkinson and Nash, *J.S.C.I.*, 1932, **51**, 265T ; *J. Inst. Petr. Techn.*, 1932, **18**, 365A.

[13] Hoffman, Lang, Berlin and Schmidt. *Brenn.-Chem.*, 1932, **13**, 161 ; *J. Inst. Petr. Techn.*, 1932, **18**, 234A.

A difference between the position isomers of cyclic compounds with several side chains could not be established. The anti-knock value of non-metallic compounds has been studied by Endo,[14] who has found that nitrogen and hydroxy compounds are anti-knocking, ethers and aldehydes are pro-knocking, while ketones and esters are intermediate. In aromatic hydrocarbons the anti-knocking tendency was found to increase when an amino or hydroxy group was added directly to the benzene ring but decreased when added directly to the side chain. According to Schmidt,[15] in the case of alcohols, the anti-knock value increases with increase in molecular weight, while the complexity of the molecule has no effect upon this property.

Beaber[16] has made several unsuccessful attempts to make lead tetra *a* naphthyl, but has found that in concentrations of 1:5000 to 1:500,000 the anti-knock effect of lead tetra phenyl is equal to that of tetra ethyl lead.

Patents on Anti-Knock Materials.

The Fuel Development Corporation[17] have patented the addition of aniline to a fuel to improve its anti-knock value and the addition of a small amount of butanol in order to prevent the separation of ingredients due to freezing or the adventitious addition of water. A mixture of gasoline or hydrocarbons of low boiling point and a cymene compound—*e.g.*, amino p. cymene—has also been advocated. [18] In a further patent amino compounds are formed in cracked spirit by treating the latter with nitric acid and then with sulphuric acid and zinc.[19] The use of aniline as an anti-knock ingredient of gasolines has also been protected by Kimball,[20] while, according to Petroff,[21] the anti-knock value of nitrogen compounds is increased by the addition of high-boiling hydrocarbon oil of high ignition temperature, *e.g.*, coal tar fractions. The following compounds have also been claimed to possess anti-knock properties[22]: alkyl or aryl esters of ferrocyanic acid, nickel, lead, cobalt, thallium, osmium, molybdenum, chromium, vanadium, or uranium cyanic acids, salts of such metallocyanic acids with organic bases, such as aniline, metal nitro prussides or carboxyl

[14] Endo., *J. Fuel Soc.*, Japan, 1932, **11**, 564; *Chem. Abs.*, 1932, **26**, 4459; *J. Inst. Petr. Techn.*, 1932, **18**, 303A.
[15] Schmidt, *Petr. Z.*, 19.3.32, **28** (10), *Motorenbetrieb*, **5** (3), 2; *J. Inst. Petr. Techn.*, 1932, **18**, 190A.
[16] Beaber, *Iowa State Coll. J. Sci.*, 1931, **5**, 320.
[17] Fuel Dev. Corpn., E.P. 379,557; *J. Inst. Petr. Techn.*, 1932, **18**, 430A.
[18] Bereslavsky Fr. P., 727,443; *Chem. Abs.*, 1932, **26**, 5201.
[19] Ellis, U.S.P. 1,867,814; *Chem. Abs.*, 1932, **26**, 5201.
[20] Kimball, U.S.P. 1,848,063; *Chem. Abs.*, 1932, **26**, 2585.
[21] Petroff. Fr. P., 714,241.
[22] Rosenstein, E.P. 349,475; *Chem. Abs.*, 1932, **26**, 2048.

cyanides, cyanides of metalloids, such as selenium or tellurium, or organic derivatives containing the SeCN group.

Rosenbaum [23] has similarly covered the use of esters of naphthenic acids, such as the butyl ester of hydroxy naphthenic acid, and also mercury compounds of naphthenic acids. The I.G. Farbenindustrie have patented [24] the improvement of liquid fuels by the addition of a small quantity of iron carbonyl, together with another metal compound soluble in the fuel or a soluble compound of boron, silicon or phosphorus. Suitable additional compounds are salts of organic acids, metal compounds of tautomeric substances and esters of suitable inorganic acids.

The use of solid aliphatic alcohols containing at least eight carbon atoms in their molecules dissolved in high-boiling hydrocarbon solvent has been advocated.[25] Riboisiere [26] has proposed aromatic amines or an azocyclic compound in association with anhydrous ethyl or methyl alcohol and in the absence of iron carbonyl or like anti-knock metal compounds.

Motor Fuel Compositions.

The Standard I.G. Company have recently patented [27] a motor fuel composed of a mixture of hydrocarbons, the flash point of which is equal to that of ordinary kerosine, and which is free from heavy substances boiling above 260° C. This patent probably refers to the high octane number safety aviation fuel recently developed by the Standard Oil Company.

According to other patents,[28] heavy mineral or vegetable oils are made suitable for use as motor fuels by the addition of an activator composed of a mixture of a diazo derivative with a nitro body or a mixture of a hydrazo with a polynitro derivative. The latter is prepared by direct nitration, *e.g.*, of anthracene or naphthalene and the diazo or hydrazo derivative by reduction of part of the nitro body.

Gullander [29] has protected a mixture of normal motor spirit with 0·25 per cent. of upper cylinder lubricant, the latter being made by the compounding of 30 parts lubricating oil, 30–40 parts tetra-hydronaphthalene and 30 parts hydrogenated phenol (cyclohexanol). Motor fuels containing explosives, such as nitroglycerin,

[23] Rosenbaum, U.S.P. 1,841,254.
[24] I. G. Farbenind A.-G., D.R.P. 539,494; *Chem. Abs.*, 1932, **26**, 1756.
[25] Deutsche Hydrierwerke A.-G., E.P. 379,231; *J. Inst. Petr. Techn.*, 1932, **18**, 382A.
[26] Riboisiere Fr. P., 710,402.
[27] Standard I.G. Co. Fr. P., 717,225; *Chem. Abs.*, 1932, **26**, 2850.
[28] S.E.B.I. Fr. P., 717,817; *Chem. Abs.*, 1932, **26**, 2850; E.P. 379,725.
[29] Gullander, E.P. 382,111; *J. Inst. Petr. Techn.*, 1932, **18**, 463A.

have been patented,[30] the explosive being dissolved in a suitable solvent and emulsified with a vegetable oil. Hydrocarbon fuels or alcohols are used to dissolve the emulsion and, with the addition of ether to facilitate ready ignition, form the finished product. Motor fuel containing alcohol or an acetone solution of acetylene has also been proposed.[31,32]

Alcohol fuels continue to be used to an increasing extent in Europe, chiefly as a result of Government decrees in an attempt to help depressed agricultural industries. An interesting review of the present situation has been given by Kaltenbrunner.[33] European motor alcohol is distilled from (*a*) agricultural products, (*b*) molasses and (*c*) sulphite pulp waste liquor. The cost of raw materials in the case of (*a*) is so high that, except by legislation, it cannot compete with other fuels. The cost of producing the fairly large quantities obtained from (*b*) in Austria, France, Germany, Hungary and Italy depends upon the price of molasses, which has been very variable. The cost of sulphate pulp waste liquor is nil, since it has no other commercial use, and in Sweden alcohol is extensively produced from this material without government aid, and retailed at 23–25 cents per gallon. Generally, where alcohol is used extensively as a motor fuel, it is not competing freely with gasoline, but has some government support through monopoly sales control of price-fixing by the State, or its admixture with gasoline is made compulsory by law. Kaltenbrunner (*loc. cit.*) has discussed the alcohol fuel situation in detail in the case of Austria, Czechoslovakia, France, Germany, Hungary, Italy and Poland.

The production of alcohol from wood waste by acid treatment has also been reviewed and details given of the Scholler-Tornesch process, which is in operation on the commercial scale in Holstein.[34] The yields said to be obtained from 100 kilos of dry wood are 60 kgs. glucose, of which 40 kgs. is fermentable and the cost 0·11 mark per litre of alcohol, based on a yield of 25 litres per 100 kgs. of dry wood.

Hubendick[35] has described the results obtained with alcohol fuels in Sweden, where "Lattbentyl," consisting of 75 per cent. gasoline and 25 per cent. alcohol, is marketed with success, and Teodono[36] has made a comparative study of alcohol, gasoline

[30] Cia Italiana Sirluppo Invenzione S.A., E.P. 358,484; *J. Inst. Petr. Techn.*, 1932, **18**, 9A.
[31] Hyeda and Kuisha, E.P. 359,291; *J. Inst. Petr. Techn.*, 1932, **18**, 9A.
[32] M. Wolff & Co., E.P. 376,286; *J. Inst. Petr. Techn.*, 1932, **18**, 340A.
[33] Kaltenbrunner, "Facts about Sugar," 1931, **26**, 67; *Chem. Abs.*, 1932, **26**, 2845.
[34] *Chem. Trade J.*, 1932, **90**, 403; *J. Inst. Petr. Techn.*, 1932, **18**, 256A.
[35] Hubendick, *Petr. Z.*, 1930, **26**, 50, Motorenbetrieb. 3–4.
[36] Teodono, Philippine Agr., 1931, **20**, 295; *Chem. Abs.*, 1932, **26**, 826.

and kerosine as fuels for tractor engines. Dietrich[37] has discussed the special precautions necessary in the mixing of alcohol fuels in order to prevent separation into two layers, while Jacque[38] has mentioned the ease with which spirits produced by the hydrogenation of coal tar dissolve ethyl alcohol. The present status of the fuel alcohol problem has been reviewed by Schweitzer.[39]

As blending agents for promoting the miscibility of alcohols and gasoline aliphatic amines have been proposed,[40] while the admixture of nitro, azo and hydrazo compounds with alcohol fuels has been suggested.[41] The stability of alcohol fuels in the presence of water has been considered by Spausta.[42]

The toxicity of motor fuels and their combustion products has received attention by Liesegang,[43] who concludes that the type of fuel used, whether gasoline or benzole or alcohols, has no influence on the toxicity of the normal exhaust products. Gasoline, considered as a mixture of paraffins, from pentane to octane, posseases definite narcotic action, the least volatile components being the most poisonous. Methanol is much more poisonous and more dangerous to use, because of its low boiling point and high volatility.

Aviation gasolines have been discussed by Banks[44] from the aero engine designers' point of view, who has also described the general history and theory of detonation and the use of tetraethyl lead as an anti-knock agent. Francis[45] has considered the gravity, sulphur content and volatility specifications of aviation gasolines.

In order to reduce the fire hazard in aircraft operation, the Standard Oil Company have investigated the possibility of manufacturing a fuel of high flash point and have been able, by the hydrogenation process, to produce a fuel having an octane number of 82·6 (without addition of knock suppressors) and a flash point of 107° F.[46] This fuel has been undergoing tests and a special carburettor has been designed to utilise the fuel to the best advantage. Tests indicate that the new fuel possesses satisfactory characteristics for aviation work, and an increase in power, combined with an appreciable drop in operating temperature, is reported for tests carried out in a single cylinder engine.

---

[37] Dietrich, *Petr. Z.*, 1930, **26** (50), Motorenbetrieb, 3.
[38] Jacque, *Compt. rend.*, 1931, **193**, 1185.
[39] Schweitzer, *Chim. et Ind.*, 1932, **28**, 12.
[40] Lantz., U.S.P. 1,869,486.
[41] *S.E.B.I.*, Fr. P. 719,708.
[42] Spausta, *Erdöl u. Teer*, 1932, **8**, 282; *J. Inst. Petr. Techn.*, 1932, **18**, 302A.
[43] Leisgang, *Z. angew. Chem.*, 1932, **45**, 329.
[44] Banks, *J.R.Ae.S.*, 1932, **36**, 127; *J. Inst. Petr. Techn.*, 1932, **18**, 162A.
[45] Francis, *Oil & Gas J.*, 4.8.32, **31** (11), 14; *J. Inst. Petr. Techn.*, 1932, **18**, 381A.
[46] Francis, *Oil & Gas J.*, 26.11.31, **30** (28), 89; *J. Inst. Petr. Techn.*, 1932, **18**, 8A.

Vapour Locking Properties of Gasolines.

The U.S. Bureau of Standards continue in their work on the vapour locking properties of gasolines, and have made numerous contributions to our knowledge on this subject during the past year, particularly with reference to automobile fuel-fed system design. Bridgeman and White[47] have considered aviation gasolines in this connection and found that the A.S.T.M. 100 ml. distillation data are adequate to give the conditions under which vapour lock occurs with propane-free fuels, but that the conditions when pump feed is used are much more difficult to predict. The effect of weathering upon the vapour locking tendencies of gasolines has been considered by Bridgeman and Aldrich.[48] The fuel line temperatures in American cars have been investigated by Bridgeman and White,[49] who have also reported upon the general principles of vapour locking and the characteristics of various fuel feed systems.[50] According to Bridgeman, White and Gary[51] solution of the vapour lock problem lies in a strict observance of the two rules, (1) keep heat out of the fuel system, (2) keep propane out of the gasoline.

Gum Formation in Gasoline and Its Prevention.

The importance of the gum contents of motor fuels has been shown in the recent work of Marley and Gruse[52] on actual engine tests. These workers have shown that gum deposits are greater from a rich gasoline-air mixture than from a lean one, and that a high air intake temperature is responsible for an increased gum deposit in the intake manifold. With increase in temperature the effect is more marked as the gum content of the fuel increases, while the combustion chamber deposits increase with temperature to a certain degree and then fall off with further rise in temperature. In general, for a fuel of any given gum content, raising the intake temperature causes a greater deposit in the intake system and less in the combustion chamber. It is suggested that by lowering intake manifold temperatures, volatile gasolines of moderate gum content might possibly be used without serious trouble from

[47] Bridgeman and White, *J.S.A.E.*, 1930, **27**, 218.

[48] Bridgeman and Aldrich, *J.S.A.E.*, 1930, **27**, 344.

[49] Bridgeman and White, *J.S.A.E.*, 1931, **29**, 447; *J. Inst. Petr. Techn.*, 1932, **18**, 34A.

[50] Bridgeman and White, *J.S.A.E.*, 1932, **30**, 129; *J. Inst. Petr. Techn.*, 1932, **18**, 121A.

[51] Bridgeman, White and Gary, *Oil & Gas J.*, 19.11.31, **30** (27), 22; *J. Inst. Petr. Techn.*, 1932, **18**, 50A.

[52] Marley and Gruse, *Ind. Eng. Chem.*, 1932, **24**, 1298; *J. Inst. Petr. Techn.* 1932, **18**, 462A.

gum deposits. According to Bridgeman[53] the factors which may influence the quantity of gum deposited in the engine manifold and on the inlet valves are: degree of vapourisation in the manifold; percentage of liquid carried into the cylinders unvapourised; temperatures of manifold walls, inlet valves and seats; temperatures of charge and manifold design.

Egloff and his co-workers[54] have contributed an important paper on the inhibition of gum formation in cracked spirits with particular reference to the relationship existing between chemical structure and inhibiting effectiveness of a large number of chemical compounds. They have found that phenol has a moderate action in preventing gum formation, but that substituted phenols carrying alkyl groups in the ortho or para positions are more effective; m. cresol, however, is no more effective than phenol, and two alkyl groups are more than twice as effective as only one alkyl group. Catechol and pyrogallol are particularly effective. The introduction of an amine (NH_2) group in any position in a phenol increases the inhibiting power, but in general the effect of a nitro group is disadvantageous. The amines are not so good, as a class, as the phenols, but diamines and secondary amines appear to be more effective than the normal monoamines. Halogen compounds, ethers, ketones, quinones, acids and acid derivatives, nitro compounds and sulphur compounds showed little inhibiting effect Tetraethyl lead had no action, while benzoyl peroxide and iron carbonyl appeared slightly to accelerate gum formation.

Numerous patents covering gum inhibitors have recently appeared, *e.g.*, tri or other polyhydroxyl benzenes, *e.g.*, pyrogallol,[55] and hydroquinone, resorcinol, orcinol, pyrogallol, 1.2.4. hydroxy benzene, or naphthol, thiourea, thio carbanilide or other reducing agents, such as stannous chloride, alkali metal acoholates, o.m. or p. phenylene-diamines, etc.[56] The proposal has also been made[57] to remove gum-forming bodies from gasolines by heating them in the presence of copper, but in the absence of any appreciable quantity of copper oxide, the gasoline then being treated with an absorbent clay. Hyman[58] claims to inhibit gum formation in cracked spirits by the addition of (*a*) ammonia or organic substitution compounds thereof to overcome autocatalysis and (*b*) catechol sufficient to inhibit further gum formation. Of particular

[53] Bridgeman, *Oil & Gas J.*, 9.6.32, **31** (3), 55; *J. Inst. Petr. Techn.*, 1932, **18**, 301A.
[54] Egloff, Morrell, Lowry and Dryer, *Ind. Eng. Chem.*, 1932, **24**, 1375; *J. Inst. Petr. Techn.*, 1933, **19**, 23A.
[55] Standard Oil Co. (N.Y.), E.P. 349,247.
[56] Standard Oil Co. (N.Y.), E.P. 348,011.
[57] Graves, U.S.P. 1,867,697; *J. Inst. Petr. Techn.*, 1932, **18**, 382A.
[58] Hyman, E.P. 364,533; *J. Inst. Petr. Techn.*, 1932, **18**, 87A.

interest is the work of Universal Oil Products, Ltd., culminating in the marketing of a gum inhibitor. The composition of this material is not known.

Dyes in Gasoline.

During the last ten years gasolines have been coloured red, blue or green by means of oxyazo dyes and those of the type Sudan G (I.) and carmin naphtha (II.). A recent paper by Lederer[59] on the solubility of some indigo dyes in oils is therefore of interest. Lederer found that indigo imparts a blue colour to oils when heated and stirred at 100–120° C. and on the addition of a small quantity of 0·5–1 per cent. of sulphuric acid, the acid being subsequently removed with sand or a bleaching earth. Indigo 04B and indigo red HR colour oils bluish green and red respectively. Of a series of indanthrene and algol dyes it was found that only indigo MLB, 4B and thioindigo red were sufficiently soluble in oil. Unbrominated and highly brominated indigo, *e.g.*, hexabromindigos. were also only slightly soluble.

[59] Lederer, *Petr. Z.*, 13.1.32, **28** (2), 5; *J. Inst. Petr. Techn.*, 1932, **18**, 86A.

Gasoline Engines and Knock Testing.

By R. Stansfield, A.M.Inst.C.E. (Member).

Engines.

Engine construction for private cars has shown considerable change as regards the distribution of sizes during the year from November, 1931, to October, 1932.

The total number of registrations has decreased by about 10 per cent. from the figures for the previous year, but, in spite of this general decrease, some of the smaller sizes have increased in numbers.

On the basis of the R.A.C. ratings all sizes down to 19 h.p. show a decrease. The 18 h.p. class shows a slight increase, but lower ratings down to 15 have decreased. The number of 14 h.p. and 12 h.p. engines has slightly increased, but the noticeable changes occur only below 11 h.p. Among the small engines there has been an increase of about 20 per cent. in the 10 h.p. size and of almost 140 per cent. in the cars of 9 h.p. The popular 8 h.p. engine shows a decline of about 25 per cent. and registrations in the 7 h.p. class have diminished slightly.

The tendency towards the use of lower engine capacities is indicated also by the fact that builders who have hitherto confined their output to high-powered and high-priced cars are, in some cases, now offering well-built smaller engines at moderate prices.

Changes in engine design are not as noticeable as developments in the transmission, suspension and body-work; but, nevertheless, improvements are steadily taking place. The suspension of the power unit in the chassis is frequently in rubber to minimise vibration and noise. Speeds are slowly increasing, and the peak of the torque curve is being raised in many examples. Much more attention is being paid to the design of the inlet manifold, both to secure good distribution and also to increase volumetric efficiency, and there is less tendency to overheat the mixture by the indiscriminate use of hot spots or exhaust jacketing.

The use of strangler for starting is rapidly being replaced by one or other of the new, so called "self-starting," carburettors in which an auxiliary jet and choke tube are brought into action when starting, these being proportioned so that a sufficiently rich mixture is obtained in the cylinders to make get-away simple in the coldest weather, and eliminating the very serious risk of excessive washing of the cylinder walls with liquid fuel, which exists with the older designs of carburettor fitted with a strangler.

While the small high-speed 6-cylinder engine is still produced in large numbers, there has been a definite revival of the 4-cylinder

engine in the smaller sizes, while some of the 8-cylinder large engines have been replaced by 6-cylinder designs.

A noteworthy development, initiated in commercial vehicle engines, is the use of inserted centrifugally cast liners of extreme hardness—an improvement which should appreciably lengthen cylinder life.

No important change has taken place in the relative numbers of types with side valves, sleeve valves, and overhead valves. Turbulent heads of one form or another are in general use with side valves, but it seems doubtful whether all such heads are as well designed as they might be.

Compression ratios tend to increase slightly, and valve material is being more carefully chosen to suit modern conditions of running at high putput and speed.

The water-cooling system of many designs has been much improved to give more even circulation, and to eliminate local boiling when the mean jacket temperature is normal for summer running, with consequent reduction in the tendency to pink. The use of radiator shutters does not appear to be increasing at present.

The magneto is still being displaced by battery and coil for ignition purposes, and the electrical system is, in most respects, being made more reliable and accessible. Automatic ignition advance control, with or without auxiliary hand adjustment, is becoming fairly general, even on the lower priced cars.

Attention to piston design, and the greater use of proprietary makes of piston, has assisted in reducing piston slap and excessive oil consumption, although there is, perhaps, a tendency to over-emphasise the importance of low consumption with consequent heavier wear of the cylinders and rings.

Little progress has been made towards the more general use of efficient oil filters or coolers, although some engines have been modified so that the sump temperature is considerably less than in previous years. This has been attained both by better jacketing of the lower ends of the cylinders and better air circulation round the oil sump.

As regards commercial vehicle engines, inserted liners are increasing in numbers, and valve materials are being improved, but attention seems to have been directed mainly to the compression ignition engine with its promise of low operating costs.

The recently issued report of the Aeronautical Research Committee does not indicate much promise of major improvements in the development of petrol engines for aircraft. During special tests an output of more than 1 b.h.p. per lb. of engine weight has been obtained, and it is expected that satisfactory engines will

become generally available weighing not more than about 1½ lb. per b.h.p. for continuous flight.

Recent years have seen a steady increase in the running time between overhauls, and it now seems that sludging, carbon deposits and ring sticking due to the effect of engine conditions on the lubricants available are the limiting factors.

The distribution problem is still serious, and it has not yet been found possible to obtain bench consumptions much better than 15 per cent. above those realised on single cylinder engines of the same type.

There seems to be a tendency to make greater use of water-cooled and evaporative-cooled engines, and this may have a profound effect on the types of petrol required, and also on the method by which such petrols are to be rated in the laboratory for anti-knock value.

As in the case of commercial vehicle engine, there is probably more activity being shown in the development ot the compression ignition engine than in the making of important changes in the well established petrol types.

Knock Testing.

Rapid progress has been made in knock testing developments during 1932. While laboratories still use a variety of types of engine and technique for this work, the C.F.R. engine has reached such a stage that few of the important laboratories, either in this country or America, are without at least one such engine, and intensive co-operative research has been and is proceeding to bring the C.F.R. plant and technique into something approaching a final form.

In the early part of the year it was agreed, as the results of about a year's experience with the present design, that the mechanical features of the C.F.R. engine were satisfactory and that the next stage of development must be the checking of test results obtained on the road against those from the test engine. Reports from various sources had shown that the correlation between road and laboratory results was by no means good (at least when considered in terms of the average results from a large number of *American* cars), the test engine showing a tendency to rate fuels too high. The deviation was most pronounced for benzole blends and cracked spirits, and least for straight run spirits.

It was, therefore, decided by the C.F.R. Committee to organise a comprehensive series of road tests for the examination of a wide range of spirits on a large number of different American cars, and also to include more than one car of a given make in certain cases. Since direct tests on the road with octane/heptane blends were not

possible, the road ratings were obtained in terms of blends of secondary standards to give the same effect as the samples.

Doubt was first expressed regarding the suitability of the usual method of road testing, viz., that of determining either the speed at which knock extinction occurred on rising speed, or the speed for knock introduction on falling speed when hill climbing. It was finally agreed that the average driver judges a spirit more by the maximum knock sound which occurs than by the speed at which knock is extinguished or at which it starts. For example, owing to carburettor adjustment and ignition advance, one spirit may not begin to knock until, say, 15 m.p.h. when accelerating, and another may begin at 20 m.p.h. The first may reach knock extinction at 30 m.p.h. and the second at 35 m.p.h., but the average driver takes notice only of the relative maximum knock intensity reached, irrespective of the speed at which it occurs, and this maximum intensity is not always found to be in agreement with either the onset or the extinction speed determination.

After discussion of the views of a large number of observers a technique of road testing was agreed upon which was based on observing the maximum knock obtained from each sample tested, and determining a blend of standard fuels which gave the same maximum knock. The test was carried out by accelerating on full throttle, when possible, from 10 to 15 m.p.h. up to as high as 50 m.p.h. if this speed was necessary for knock extinction, and all results were checked by different observers at least once.

The tests showed that not only did different makes of car rate given spirits differently, but that even two cars of the same make and type might give widely different ratings to a sample. The total spread of ratings was so great that, in an extreme case, a car might rate a sample almost equal to the lower anti-knock value standard, or, alternatively, almost equal to the higher value standard, depending on the adjustments and general condition of the engine. The standards differed by about 28 octane numbers in laboratory rating.

A range of 10 to 14 octane numbers was not at all uncommon on a given sample and car.

The results from the entire series of tests were tabulated and averaged arithmetically, and these averages, it was decided, must be accepted as representative ratings from road tests.

It should be emphasised that no laboratory method of practicable value can ever do more than give agreement with the average of road results, and that individual road tests may frequently show differences up to several octane numbers in either direction from the mean value indicated by suitable laboratory figures.

Until this time the standard C.F.R. engine technique specified

that the engine was to be run at 600 r.p.m. with evaporative cooling at 212° F., and without either inlet air heating or mixture heating. With the exception of the jacket temperature it is obvious that all these conditions are much less severe than those which obtain in an engine on the road with its higher speed at miximum knock, its generally poorer design of combustion chamber as regards local hot spots, and, frequently, its excessive mixture heating and large manifold volume in which considerable fuel evaporation can take place.

The original C.F.R. technique, known as the Research Method, was used for the preliminary rating of the samples tested on the road. The mean deviation between the road and laboratory tests was found to be about 10 per cent. of the higher value reference fuel in the lower, corresponding to about 2 to 3 octane numbers. There was, however, a deviation on selected samples from about 0 to 10 numbers depending on the nature of the sample.

The direction of the variations and their amounts confirmed that the laboratory conditions by the Research Method were not sufficiently severe to reproduce road conditions, and tests were, therefore, made to determine which of several variables it was best to adjust in order to improve the agreement.

The methods explored were :—

(*a*) Heating the intake mixture beyond the carburettor while keeping the jacket temperature at 212° F.

(*b*) Increasing the jacket temperature by using ethylene glycol as the coolant.

(*c*) Throttling the mixture beyond the carburettor choke tube.

(*d*) Throttling the exhaust by altering the valve timing and so leaving a greater percentage of hot residuals in the cylinder.

Each of these variables was examined at speeds of 600, 900, 1000 and 1200 r.p.m., and it was decided to adopt 900 r.p.m. as the most satisfactory speed instead of the 600 r.p.m. speed used for the Research Method.

Correlation was obtainable by each of the four methods mentioned, but it was found that the throttling method severely restricted the upper range of the engine, and that the exhaust throttling method was not easily reproducible under practical manufacturing conditions on account of extreme sensitivity to change of valve tappet clearance when the valve closed sufficiently early.

The methods of mixture heating and additional jacket temperature were both satisfactory, the latter necessitating the use of ethylene glycol and water to boil at 330° F., together with a certain amount of mixture heating.

It was finally decided to adopt the simpler method of regulation on mixture temperature only, it being understood that the recorded mixture temperature was, in many cases, only an indication of true conditions and depended for reproducibility on careful standardization of the mixture heater, its container and the thermometer used for temperature indication.

The new technique, known as the "C.F.R. Motor Method" for conducting anti-knock tests, differs from the Research Method in five respects as follows :—

(*a*) Speed 900 r.p.m. instead of 600 r.p.m.

(*b*) Mixture temperature 300° F. instead of uncontrolled, and dependent on laboratory temperature.

(*c*) Spark advance at 5 : 1 compression ratio, 26 degrees before top centre, instead of 22½ degrees, the control still being automatic with the original link gear.

(*d*) Shrouded inlet valve to give turbulence. This valve reduced volumetric efficiency slightly.

(*e*) Elimination of the circulating water pump and improvement of the condenser.

The measure of agreement reached with average road conditions by this technique was extremely good, and justifies the adoption of the Motor Method, at least on the evidence so far available. Certain details such as the correct throttle position (which was 75 degrees scale reading for the Research Method) have yet to be settled, but the method is recommended by the C.F.R. Committee for the determination of knock ratings of spirits from April 1st, 1933.*

While this method of rating marks a distinct improvement over any previous technique in that it demands the use of a standardised technique and plant and is based on recent road tests, it should not be assumed that no further changes will be made. The C.F.R. Committee points out that alterations to automobile engines in the direction of higher engine speeds and smaller cylinders, and developments in combustion space design and cooling, may mean that revisions will be necessary periodically, such revisions being controlled by results of further road tests. It is also desirable that British cars, especially those of small capacity running at high speed, should be included in a series of road tests, and the average results compared with tests both on American cars and by the C.F.R. Motor Method of Rating. There is evidence that the Motor Method depreciates some fuels too much for the average small engine used in

* Since the above was written the throttle position has been standardized at 90 degrees scale reading.

this country, and if this is shown to be the case it may be desirable to test at lower mixture temperatures for the market concerned.

As regards laboratory ratings for anti-knock values of aviation spirits, the position cannot be described as anything less than chaotic, either here or in America. While ratings on the S30 engine at jacket temperatures from 150° C. to 190° C. have been stated to give agreement with practice in some cases, there is a divergence of opinion as to the suitability of these conditions, and some evidence that they depreciate many fuels too much to suit British air-cooled engines. They are certainly far too extreme for water-cooled aero engines.

Work is being done in both countries towards a solution of this difficult problem, and, while there is now some promise that a solution will shortly be reached for Britain, any conclusion on this important question would at present be premature.

Kerosine and White Spirit.

By S. T. Minchin, B.Sc., A.I.C. (Associate Member).

Relatively little work specifically on the subjects of kerosine and white spirit has been published in the period under review. As regards refining, much progress has been made, but such improvements are more in the nature of general methods applicable to a whole range of products, and are, therefore, better dealt with under refining methods. Only methods of specific application to these products, or of outstanding interest as regards yield or quality of product, are reviewed under this section. The same applies to the general examination of the physical properties of lighter petroleum distillates.

The "tendency to smoke" test, that is being considered by a special Sub-Committee of the Institution, and which was referred to in last year's survey,[1] is nearing completion. A lamp for the test was exhibited at last year's exhibition. This lamp is being improved, and a tentative method of test has been drawn up. It is hoped that the test will be included in the new edition of Standard Methods.

Burning Properties, and Their Relationship to the Method of Refining.

Dănăilă and Stœnescu[2] have extended their study on the effect of various refining methods on the burning properties of Rumanian kerosine. The method of experimentation was to prepare synthetic lamp oils from an oil substantially free from olefinic and aromatic hydrocarbons to which was added known quantities of olefine and aromatic hydrocarbon mixtures. The effect of refining treatments with sulphuric acid, liquid sulphur dioxide and floridin was also examined. The illuminating power was then determined as described in last year's review. The authors conclude that the presence of aromatic hydrocarbons does not decrease the illuminating power of the oil since the illuminating power of the "aromatic and olefine free" base is less than that of the synthetic blends. The authors again restate their previous conclusion that only after a certain maximum addition of aromatics (30–35 per cent.) does the illuminating power decrease. They also state that oils free from aromatic and olefinic hydrocarbons have less illuminating power than unrefined and synthetic illuminating oils containing aromatic hydrocarbons. The fact that sulphuric acid treatment (from 1–3 per cent. of 98 per cent. acid) usually gives a product having a higher illuminating power than the unrefined

[1] Woodrow, *J. Inst. Petr. Techn.*, 1932, **18**, 357.

[2] Dănăilă and Stœnescu, *Petr. Zeit.*, 27.4.32, **28** (17), 1–4; *J. Inst. Petr. Techn.*, 1932, **18**, 212A.

product, although it contains less aromatics and olefines, is put down to the removal of asphaltic substances by the acid. The authors appear to be of the opinion that asphaltic and tarry substances are the main cause of unsatisfactory burning. Floridin is found to have little effect on illuminating power. It is further suggested that high aromatic content kerosines need special lamps.

These views have been questioned by Grote and Hundsdörfer,[3] who consider the Louchaire lamp (used by Dănăilă and Stœnescu) and the synthetic oils to be unsatisfactory for such general deductions. They further state that they were unable to confirm Dănăilă and Stœnescu's results. Grote and Hundsdörfer also employed Rumanian kerosine but used both the Louchaire and the Cosmos lamps, fitted with constant low level devices. They determined illuminating power and flame heights, over certain time intervals, of unrefined kerosine, kerosine to which liquid SO_2 extract had been added in various proportions, and kerosine after increasingly stringent liquid SO_2 treatments. They also elaborated a smoke test which is carried out by observing the deposition of soot on chimney and a movable disc after the lamp has been left burning under specified conditions for a certain period. They conclude that aromatic removal gives cleaner burning, and state that the property of a kerosine to burn free from smoking and with a pleasant odour was as important as illuminating power.

These two communications are an interesting comment on the state of exact knowledge on the burning of kerosine. There is, of course, little doubt that a non-smoking kerosine is generally preferred ; whilst, also, there is little doubt that aromatic kerosines can be burnt satisfactorily in suitable lamps (*vide* Kewley and Jackson,[4]) and also that when such kerosines are burnt they give excellent illumination and brilliant flames. The conclusion seems to be that the average lamp is more suitable for non-aromatic oils, and this is partly due to the fact that aromatic kerosines, even in specially designed lamps, are very susceptible to slight changes in burning conditions ; partly due to the fact that the first kerosines were mainly non-aromatic ; and partly due to the fact that lamps suitable for non-aromatic oils are simpler in construction and cheaper to manufacture.

A very interesting communication bearing closely on these points has been made by Baker,[5] who deals with the subject from the view-point of signal lamps. Baker points out that for signalling the beam candle power is the important factor, and

[3] Grote and Hundsdörfer, *Petr. Zeit.*, 13.7.32, **28**, 9-14 ; *J. Inst. Petr. Techn.*, 1932, **18**, 341A.

[4] Kewley and Jackson, *J. Inst. Petr. Techn.*, 1927, **13**, 372.

[5] Baker, *Inst. Railway Signal Engineers*, May, 1932.

that the beam candle power is dependent on the brightness of the flame rather than the gross candle power. Moreover, it is the brightness of that particular portion of the flame at the focus of the optical system. It follows from this, that, other things being equal, a kerosine giving a high flame brightness is to be preferred. Baker then proceeds to calculate the brightness of various signal oils when burnt in a signal lamp, and shows that the brightness varies greatly for different oils. Unfortunately, the figures are calculated from data not specially compiled for the purpose and published elsewhere,[6] and it is difficult to see from the analyses of the oil any underlying reason for the variation in brightness. It is very much to be hoped that more complete data on this interesting subject will be published; in the meantime, Baker's work appears to indicate that for the utilisation of kerosine for signalling, the kerosine should be refined for high brilliance (and, of course, long time burning) rather than mainly for non-smoking properties, as is the case when kerosine is used for general illumination. The paper also points out that brilliancy measurements of kerosine flames need an illumination determination, and that there is no such standardised method available. Various tentative specifications and methods of test are also suggested.

With regard to the design of burners for kerosine, although these do not properly come within the scope of this survey, it is useful to note the general trend of lamp design as this indicates fresh knowledge on the combustion of kerosine. Thus, a patent is taken out for supplying primary air at different heights in the flame zone[7]; another is claimed for a device for changing the direction of air flow and increasing its rate in a uniformly dispersed manner[8]; and a method for moving the wick to the optimum position for producing a smokeless flame is protected.[9] The inventions tend to show that one of the present trends in burner design is to realise the utmost efficiency in the combustion of the fuel by allowing the air to be distributed uniformly over the flame surface.

Refining.

Various references to the beneficial effect of hydrogenation on the refining of kerosine have been made.[10, 11, 12] In the last mentioned,[12] Gohr and Russell state, in a general review, that a high sulphur content, off colour burning oil distillate gave a liquid yield of 100–105 barrels per 100 barrels of feed stock, that

[6] *Report Com. XI. of Sig. Sect. of Amer. Railway Ass.*, November, 1923.
[7] E.P. 369,196; *J. Inst. Petr. Techn.*, 1932, **18**, 212A.
[8] E.P. 378,086; *J. Inst. Petr. Techn.*, 1932, **18**, 464A.
[9] E. P. 370,918; *J. Inst. Petr. Techn.*, 1932, **18**, 258A.
[10] Rev. Petr., 1932 (468), 372; *J. Inst. Petr. Techn.*, 1932, **18**, 183A.
[11] E. P. 360,201; *J. Inst. Petr. Techn.*, 1932, **18**, 53A.
[12] Gohr and Russell, *J. Inst. Petr. Techn.*, 1932, **18**, 599.

contained 68–85 per cent. of burning oil. This burning oil meets specifications as to colour and smoking tendency.

G. M. Kirkwood[13] describes a method of desulphurisation by hypochlorite; Smith[14] claims sulphur removal by passing the vapour and steam into a tower containing a cyanised coke mixture.

Zakharenko and Mirzakuliev[15] have examined in detail the effect of sulphuric acid treatment on various Russian kerosines. Their results seem to show that the method of application makes relatively little difference, and that in certain instances a drying wash with acid sludge is practicable.

The steam distillation of acid sludge from Shukkôkô (Japanese) kerosine at 200–220° C. has yielded 33 per cent. of aromatic distillate. Naphthalene, m-xylene, psuedocumol and mesitylene were isolated.[16]

L. Edeleanu[17] has given an interesting survey of the development of the process bearing his name, and included various detailed and informative tables showing the effect of this treatment on kerosine as regards illuminating power, specific gravity, sulphur content and uses of extract. Flow diagrams are included. This survey is a most valuable one, both on account of its source and the comprehensive nature of the summaries regarding the chemistry, physics and economics of the process.

White Spirit.

Very little of outstanding interest to the petroleum industry has come under review. There have been various endeavours in France to tighten turpentine specifications.[18, 19] Dupont and Barraud[19] have claimed the superiority of turpentine over white spirit generally, and Blin[20] specifically for submarine paints and varnishes.

Raciński[21] has described a method for detecting gasoline and kerosine in small quantities of turpentine. Wolff and Rabinowiez[22] have investigated the dependence of viscosity, drying time and hardness of varnish and paint films, on the use of benzine, benzine and white spirit, decaline and American turpentine. Only slight differences occur.

---

[13] Kirkwood, *Petr. Eng.*, February, 1932, **3** (5), 108; *J. Inst. Petr. Techn.*, 1932, **18**, 161A.
[14] E.P. 371, 394; *J. Inst. Petr. Techn.*, 1932, **18**, 259A.
[15] Zakharenko and Mirzakuliev, *Neft. Kharzy*, **20**, 203–6.
[16] *J. Soc. Chem. Ind.*, Japan, **34**, Supp. binding 347–8.
[17] L. Edeleanu, *J. Inst. Petr. Techn.*, 1932, **18**, 898.
[18] *4iem, Congrès de Chimie Industrielle.*
[19] Dupont and Barraud; *Chimie et Ind.*, Special No., March, 1932; 641–5.
[20] Blin, *Mat. Grasses*, 1932, **288**, 9472–3; *J. Inst. Petr. Techn.*, 1932, **18**, 312A.
[21] Racinski, *Wiadomasci Farm.*, 1931, **59**, 215–16.
[22] Wolff and Rabinowicz, *Farben Zeit.*, 1932, **37**, 1050–2.

Lubricants and Lubrication.

By A. R. Bowen, D.Sc., Ph.D., F.I.C. (Member).

The period under review has seen activity in all branches of the preparation and application of lubricants, and side by side with the more fascinating subjects of synthetic oils and special lubricants, there is steady progress in investigation on the production of the highest grade of lubricating oils possible from a crude oil. The technological aspect of lubricating oil production will be reviewed more fully elsewhere, together with general refinery technology, but the work of one authority—namely, W. L. Nelson—must receive some mention under this section, as his recent contribution follows, and depends so largely on, the data accumulated on a crude oil on the laboratory scale. The contribution referred to is on vacuum equipment and design.[1] It is pointed out that designers of such equipment have universally agreed that a pipe-still containing a large proportion of radiant heat absorption surface is desirable. As is now well-known, overheating of the lubricating oil must be avoided, and the two methods suggested to do this are: the increase of the velocity of the oil past the heating surface or the decrease of the rate of heat absorption per unit surface.

The tower and plate design govern the fractionation which the lubricating oil stocks undergo, which is of vital importance in facilitating the subsequent operations of de-waxing and treating. The problem of vacuum fractionation is not a simple one for the following three reasons: firstly, the large ratio of vapour to liquid; secondly, the structural difficulties involved in keeping the pressure drop low and at the same time without exceeding reasonable size limits, and, finally, the low pressures that must be maintained. The diameter of the tower is thus, necessarily, great, and the reflux liquid must traverse a long path across each tray. This may lead to channelling of the reflux liquid and special features are introduced in the design of the plates. As regards the reflux and partial condensers, since the volume of vapours under vacuum conditions at the top of the tower is large, designers have often advocated the withdrawal of most of the reflux heat by reflux condensers placed in the top of the tower. Thus the vapour lines leaving the tower are reduced in size, and the friction loss through the vapour line can be more easily reduced. In this paper a figure is given showing the laboratory data, including the true boiling point distillation curve, the gravity and viscosity, at 100° F. and

[1] *Petr. Eng.*, Feb., 1932, **3** (5), 24; May, 1932, **3** (8), 59; *J. Inst. Petr. Techn.*, 1932, **18**, 177A, 260A. See also R. S. Danforth, *Refiner*, 1932, **11**, 408; *J. Inst. Petr. Techn.*, 1932, **18**, 383A.

210° F., of each cut at the mid-per cent. point of the cut, and the flash vaporisation curves of a typical Mid-Continent reduced crude oil: the significance of these characteristics was discussed in a previous paper by this author.[2] A diagram is shown of a general arrangement of a vacuum tower, and a figure is given on the approximate distillation curves and flash vaporisation curves of a wax distillate (and gas oil) and cylinder stock.

The advantages of the continuous acid treating method for the refining of lubricating oils, as outlined by E. Petty,[3] may be summarised as follows. The practice of air blowing as a means of mixing lubricating oil and acid is stated to give inefficient mixing, over-oxidation, bad odour and colour in the distillates, owing to solution in the oil of oxidised compounds. Mechanical agitation has made much improvement, but the separation of the sludge from the oil presents some problems. This separation can be divided into two stages, sludge separation and "pepper" settling. With the former, if a proper temperature, time and thoroughness of mixing are used, the acid will act purely as a solvent for the asphaltic compounds. The acid in the sludge, however, will continue to react with the asphaltic material, generating sulphur dioxide which will rise through the oil and result in the formation of a pepper sludge. This sludge is drier, lighter and more finely divided than the first sludge, and its presence results in an oil of high acidity and darker colour. The mixing, therefore, must be carried out under conditions which will give the minimum tendency to vaporise the acid. The temperature of treatment should be such that the oil is of suitable viscosity, and that the optimum acceleration of reaction is obtained. Temperatures above 140°–160° F. cause evolution of acid vapours and, hence, pepper sludge. Normally, the time factor will vary from 6–12 minutes. From two standpoints the acid must not vary in proportion when treating with the centrifugal continuous method: firstly, with varying proportions the result will be that of under- or over-treating with an uncertain average or composite sample; and, secondly, the solution of acid and asphalt varies in proportion to percentage.

The effect of concentration on the refining of a lubricating oil by adsorption has been studied by H. J. Tormey, F. L. Koch and J. O'Connor.[4] The amount of adsorption was measured by the percentage of colour removal produced by percolation through a

[2] *Petr. Eng.*, 1931, **2** (7), 163.
[3] *Refiner*, 1932, **11**, 13; *J. Inst. Petr. Techn.*, 1932, **18**, 88A; cf. E. W. Zublin, *Refiner*, 1932, **11**, 558; *Oil & Gas J.*, 17.11.32, **31** (26) 74; *J. Inst. Petr. Techn.*, 1933, **19**, 54A.
[4] *Refiner*, 1932, **11**, 23; *J. Inst. Petr. Techn.*, 1932, **18**, 88A.

standard clay, in a laboratory filter, of solutions of a lubricating oil of various concentrations in benzene and naphtha, respectively.

For the de-waxing of lubricating oils, methylene chloride has been suggested by P. J. Carlisle and A. A. Levine.[5] From the results of their experiments, it appears that methylene chloride satisfies the requirements for an ideal de-waxing solvent. Its selective solubility at low temperatures is high, giving an oil with nearly the same pour-point as the chilling temperature.

Grease manufacture has been the subject of two useful papers by W. T. Sieber,[6] and B. H. Lincoln and P. S. Showell[7] respectively; in the former paper the selection and handling of grease plant raw materials is considered, and the second paper is concerned with modern devices in grease plant.

The trend of the development of the production of synthetic lubricants, especially by the polymerisation and condensation of olefines, is most readily observed from the patent literature. In the report on Lubricants for 1930–1931, in this Journal, mention was made, briefly, of the synthetic oil "Paraflow," marketed for lowering the pour-point of paraffin-base oils. Since that time more details are available and great interest has been shown in this novel product.

The chief points about this synthetic hydrocarbon oil have been reviewed recently.[8] It is claimed that the presence of some wax in an oil is desirable, apart from its undesirable crystallisation tendencies. It has been found that small quantities of "Paraflow" (about 1 per cent.) lower the pour-point of a natural lubricating oil—*e.g.*, from 30–35° F. to 0° F., without impairing its other desirable characteristics. The presence of a small amount of "Paraflow" results in a marked decrease in the size of the wax crystals of a paraffin distillate, giving a result similar to that of a protective colloid. Other substances, such as ceresin and asphalts, can decrease the crystal size of paraffin wax but do not lower the pour-point. By some such effect as adsorption, a reduction of the amount of oil normally retained by wax crystals is caused, and the dual function of reducing the crystal size and the amount of oil adsorbed is considered most likely to be the basic mechanism of the action of "Paraflow." Because of the absence of long interlocking crystals, stocks containing petrolatum are less responsive to "Paraflow" than distillates containing more crystalline forms of wax. "Paraflow" is not claimed as a competitor of the conventional centrifuge de-waxing equipment,

[5] *Ind. Eng. Chem.*, 1932, **24**, 384; *J. Inst. Petr. Techn.*, 1932, **18**, 168A.
[6] *Petr. Eng.*, 1932, **3** (7), 72; *J. Inst. Petr. Techn.*, 1932, **18**, 259A.
[7] *Oil & Gas J.*, 24.3.32, **30** (45), 26; *J. Inst. Petr. Techn.*, 1932, **18**, 168A.
[8] *World Petroleum*, 1932, **3**, 428.

but, in reality, as a complement to the centrifuge. Thus, it is used economically to lower the pour-point in conjunction with centrifugal de-waxing—*i.e.*, de-waxing to a moderately high pour-point and using "Paraflow" to bring the pour-point down to zero. The manufacture of "Paraflow," by the condensation of chlorinated paraffin wax with an aromatic hydrocarbon, such as naphthalene, is an application of the Friedel-Craft reaction. For the period of less than a year, it is stated that sufficient "Paraflow" has been sold to treat more than 40,000,000 gallons of motor oil.

The general theories of lubrication and the physical and chemical aspects of lubricating oils and greases are constantly under consideration, and some work in this direction has been published in the period under review. The viscosity and resistance to flow of viscous mineral oils have been investigated by A. Gemant,[9] who showed that mineral oils possess slight elasticity resembling that of colloidal solutions, and that their resistance to motion in tubes is influenced by both viscosity and limiting elasticity or resistance to flow. The question whether the loss of viscosity in lubricating oil by dilution is a criterion of lubricating power has been reviewed by M. Roegiers,[10] and criticisms are made of Tausz and Staab's claim in this connection.

The adherence of lubricants to metals has been studied by A. Boutaric and R. Amiot.[11] The rate at which various oils flow off uniform-sized plates of copper, iron, aluminium and an unoxidisable steel, determined by plotting weight of adhering oil against time, decreases, and the limiting weight ($\overline{\wedge}$) increases, with the viscosity of the oil, but $\overline{\wedge}$ is slightly greater for vegetable oils than for mineral oils of equal viscosity. Expressions of results obtained by centrifuging are given, and the behaviour of non-acid oils upon different metals is discussed. The variation in melting point of mineral oils, accompanied by change of state or the "tempering" of oils, has been the subject of investigation by P. Woog, E. Ganster and F. Coulon.[12] It was shown that certain mineral oils, congealed at –85° C., showed different melting points according to the rate of cooling, the time during which the oil was kept at the congealing temperature, and the temperature of the bath in which the fusion took place, the melting point tending to a constant value as the rate of cooling was reduced and the time of maintenance at the temperature of congelation prolonged—*i.e.*, as the oil was more completely "tempered." It was concluded that the oil solidifies in two forms: (*a*) vitreous,

[9] *Sitzungsber. Preuss. Akad. Wiss.*, Kl., 14, 1932.
[10] *Angew. Chem.*, 1932, **45**, 320.
[11] *Compt. rend.*, 1931, **193**, 593.
[12] *Compt. rend.*, 1931, **193**, 850.

of lower, and (*b*) crystalline, of higher, melting point, and that time is required for the conversion of (*a*) into (*b*).

Capillary flow under high pressure as regards the theory of non-uniform viscosity, illustrated by experimental data, has been discussed by M. D. Hersey and G. H. S. Snyder.[13] A theory is developed for the flow of liquids in capillaries under pressures sufficiently high to cause an appreciable change in viscosity. The results are expressed in the form of Poiseuille's law, with a correction factor. The mathematical analysis leads to several methods for determining the viscosity-pressure characteristics of lubricating oils by observing the efflux from a long metal capillary into the atmosphere. Results are given for greases and castor oil at, approximately, 45,000 lb., per sq. in., pressure. The flow of lubricating greases has been studied by M. H. Arveson,[14] who forced greases through a capillary by a piston moving at a constant speed. The pressure of the grease at the point of entry to the capillary was measured. Curves of apparent viscosity-rate of shear (reciprocal sec.) are given. The apparent viscosity of greases made from the same oil, at given rates of shear, increases with increasing soap concentrations, decreases with increasing rate of shear, and approaches a value of the same order of magnitude as, but higher than, that of the oil in the grease. The nature of the curves suggests one general relation for each type of grease.

The application of lubrication principles in machine design has received some attention during the year. The fundamentals of automotive lubrication have been reviewed by H. C. Dickinson and O. C. Bridgeman.[15] These authors discuss journal bearings, ball and roller bearings and gears from the point of view of available information on the relations between the independent variables —lubricant characteristics, operating conditions and design factor—and a performance factor as the dependent variable. The treatment of journal bearings is mostly mathematical, and is based on information obtained at the Bureau of Standards during the last few years, attention being confined entirely to the *régime* of thick-film lubrication. A general equation relating the coefficient of friction and ZN/P is formulated to include the effects of end-leakage and eccentricity, and it is further expanded to account for the ratio of clearance to diameter, thus :—

$$f = a + \mathrm{K}\,[(\mathrm{ZN/P})\,(\mathrm{D/C})],$$

where f = coefficient of friction, Z = absolute viscosity, N = speed in r.p.m., P = load per unit of projected area, a = a constant covering

[13] *J. Rheology.*, 1932, **3**, 298.
[14] *Ind. Eng. Chem.*, 1932, **24**, 71 ; *J. Inst. Petr. Techn.*, 1932, **18**, 87A.
[15] *J.S.A.E.*, 1932, **31**, 278 ; *J. Inst. Petr. Techn.*, 1932, **18**, 344A.

the effects of end-leakage and eccentricity, and K = a dimensional constant. In addition the equation :—

$$H = PN\,[a + K\,(ZN/P)\,(D/C)]\,\overline{\wedge}\,LD^2$$

(where L = length and D = diameter of bearing), is deduced for the purpose of evaluating the power (H) dissipated in the bearing, when the values of ZN/P are not too close to the minimum point on the *f*ZN/P curve.

A conclusion is made that the heat generated is removed from the oil-film to the metallic parts of a bearing at a very rapid rate, and hence the main problem in cooling a bearing is to remove heat from the metallic parts rather than from the oil-film. The suggestion is proffered that an answer to the cooling problem is the use of an oil cooler and a system which will provide, in addition to lubrication, an effective heat-transfer from the metal parts to cooled oil. This would permit the designing of bearings for operating at higher and safer values of ZN/P. With reference to properly designed ball and roller bearings, the authors state that the main consideration appears to be the length of time that the steel will resist fatigue failures. Use of high-tensile steel and special heat treatment have resulted in long bearing life. With gears, on the other hand, the matter of wear and seizure is of the utmost importance, friction being of little interest except in so far as it gives an indication of operating temperatures at the gear teeth. Special extreme-pressure lubricants are necessary, in many cases, to prevent rapid scoring, which soon leads to seizure.

The subject of film lubrication of journal bearings has also been studied by R. O. Boswall.[16] The main object of the experimental investigations described was to determine the conditions governing the effective operation of a film-lubricated journal bearing, fitted with an ordinary fixed brass, and to obtain information on : (*a*) the influence of length of arc subtended by the brass upon the formation and maintenance of the film ; (*b*) the effect of loading the brass eccentrically ; (*c*) the effect of alterations in load and speed upon the position taken up by the journal relative to the brass ; and (*d*) the magnitude of the film thickness and frictional resistance for various working conditions.

It was concluded that for satisfactory lubrication of the ordinary journal bearing : (1) The journal must be capable of setting itself in such a position that (*a*) the resultant film pressure is equal in magnitude to the load, and (*b*) the lines of action of the load and resultant film pressure can coincide. (2) The criterion ZN/P should, in all cases, exceed unity, and preferably have a greater value than two. (3) With low values of ZN/P and small arcs

[16] *Engineering*, 1932, **133**, 527 ; *J. Inst. Petr. Techn.*, 1932, **18**, 261A.
[17] *J.S.A.E.*, 1932, **31**, 371 ; *J. Inst. Petr. Techn.*, 1932, **18**, 430A.

of contact, the film thickness will be small, and special care must be taken with regard to the mechanical finish of the bearing surfaces. (4) Bearings should be designed so that the effective film length does not exceed 105° in the case of clearance brasses, and 60° in the case of bedded brasses. (5) Eccentric loading and the provision of champhered inlet and outlet passages materially improves the conditions of operation and encourages the formation of a thicker film. The results are strictly applicable only to a bearing which has unrestricted vertical freedom.

Journal-bearing friction in the region of thin-film lubrication has been reviewed by S. A. McKee and T. Rv. McKee.[17] Recent evidence has indicated the concept of a load-carrying oil-film to form a basis for the design of journal bearings, and that the behaviour of the bearings follows the general lines indicated by theoretical analyses of the mechanics of the complete film of lubricant. The present use of higher speeds and pressures (resulting in the need for greater rates for heat dissipation and in the greater possibility of oil-film breakdown) has raised the doubt whether or not the criterion for bearing design should be based strictly on the characteristics of fluid-film operation. Their paper deals, therefore, with the effect of variables under the conditions in which a complete film of the lubricant is not maintained between the surfaces. A friction machine was used to obtain experimental data. The effects of changes of load, speed, viscosity, bearing metal and bearing surface, were studied.

It was further shown that if f is plotted against $ZN/\sqrt{P}$, all the data for a given bearing fall, within reasonable limits, upon the same curve. Accordingly, $f = \phi\ (ZN/\sqrt{P}) + b\ [(ZN/P)\ (D/C)]$ presumably would represent bearing friction in both the stable and unstable regions of lubrication, but further work is necessary before this equation can be considered general.

The bearing-load analysis and permissible loads, as affected by lubrication in aircraft engines, are the subjects of a paper by F. L. Prescott and R. B. Poole.[18] The paper presents the results of analysis of the leading aircraft designs, together with graphical and analytical methods of analysing bearing loads. The analytical method, using empirical constants, is derived from the long, tedious, graphical method, and enables bearing loads to be calculated quickly, with sufficient accuracy for all engine design purposes.

A comprehensive account of the lubrication factors in Diesel engines has been put forward by A. M. Tode[19] in three papers on

[18] *J.S.A.E.*, 1931, **29**, 296, 379; *J. Inst. Petr. Techn.*, 1932, **18**, 12A.
[19] *Petr. Eng.*, Oct., 1931, **3** (1), 81; Jan., 1932, **3** (4), 26; Mar., 1932, **3** (6), 74; *J. Inst. Petr. Techn.*, 1932, **18**, 14A, 166A, 167A.

the lubrication of Diesel air compressors, the lubrication of Diesel engine power cylinders and on the lubrication of Diesel engine bearings, respectively. The rate of oxidation of the lubricating oil in the Diesel engine power cylinders is stated to be controlled, within limits, by correct arrangement of piping, cylinder injection tube, size of lubricating oil ports in the cylinder liner and design of the mechanical lubricator.

The subject of extreme-pressure lubricants is receiving the attention it inherently deserves. Several important communications on this subject have appeared. H. C. Mougey and J. O. Almen[20] point out that failures of gears in rear axles of automobiles are mainly due to failure of gear teeth by breakage or by pitting or scoring of gear teeth. These failures can be remedied to a certain extent by improvements in material, design and heat treatment, but scoring is the factor which may be expected to set the limit on loads which may be transmitted through gears. The research laboratory of the General Motors have, for the last four years, been engaged in studying the properties of high-pressure lubricants. In automobile gears, the pressure between gear teeth may reach values as high as 400,000 lb. per sq. in., with rubbing velocities ranging from 0/300 ft. per min., between convex curvatures poorly adapted to maintain a lubricating film. It is inconceivable that even the most viscous oils and greases can be retained between the surfaces of the teeth in a sufficiently thick film to prevent metallic contact, especially as operating temperatures of over 210° F. are common. Scoring conditions are reached in hypoid gears earlier than in the spiral bevel type for equal loads. It is concluded that the limit of capacity of ordinary oils is being fast approached, and a special machine has been built in their laboratory for testing purposes, which is described. A commercial extreme-pressure lubricant on test behaved like an ordinary oil as long as the oil-film was maintained; the friction then rose more gradually with increased pressure, and after a certain pressure was reached, tended to fall off again, indicating that high pressure lubrication is accomplished by some other medium having properties different from oil as used in ordinary film lubrication. Addition of lead soap alone did not seem to increase the load-carrying capacity of mineral oils, but in conjunction with sulphur gave improved performance in the transition stage, when compared with addition of sulphur only. The results indicated that load-carrying capacity was due to formation of a separate film, not of oil, but of some material formed directly on the surface of the steel. Various chemical substances were, therefore, tried, and certain esters were found to be slightly more

[20] *Oil & Gas J.*, 1931, **30** (26), 109; *J. Inst. Petr. Techn.*, 1932, **18**, 13A.

effective than mineral oils; 1 per cent. of carbon tetrachloride added to a mineral oil and dichlorethyl ether alone were both found to provide effective extreme-pressure lubricants, and it is believed that this is due to the formation of an iron chloride on the surface of the steel. The authors state that laboratory results must be carefully interpreted and related to service, since variations in method of test have given contradictory results.

Lead oleate and border-line lubricants have been studied by M. Reswick,[21] who terms the border-line the point at which a straight mineral oil breaks down, due to pressure and permits the rubbing surfaces to come into metallic contact. In tests, it was found that a mineral cylinder oil broke down at 8,000 lb. per sq. in. pressure, whereas a lead oleate lubricant of the same viscosity only broke down at 45,000 lb. per sq. in. Whilst other ingredients may operate as efficiently as lead oleate, it is stated that the latter, when properly incorporated in a lubricant, is the safest to use. The limited application of these lead oleate-containing lubricants, and the variations in viscosity of the compound necessary with the duty, are noted. Low viscosity is suggested when the lubricant is to be used for light duty. Medium viscosity is required for medium sized, gear-reducer units (spur, bevel, herring-bone and planetary types, etc.). The heavy viscosity type is used in the automobile and other industrial spheres—*e.g.*, worm-gears of every size, reduction gears (hypoid), screw-downs on rolling-mills and in mechanical crane brakes of the disc type. Extra-heavy viscosity lead oleate lubricants are used in the steel industry (rolling-mill pinion gears and bearings and all gears subjected to shock and heavy over-loading).

The findings of the survey carried out by the Lubricants Research Sub-Committee of the S. A. E., on the characteristics, use and testing of extreme-pressure lubricants have been stated recently.[22] The manufacture of lead soaps with respect to lubricants has been discussed by W. T. Sieber.[23]

The original classification of free-wheeling lubricants has been modified by the S. A. E. Lubricants Division,[24] and certain lubricating oil specifications for use in Kansas have been described by J. P. Calderwood.[25] W. T. Ziegenhain[26] has discussed the changes in properties of marketed lubricating oils, and analyses of lubricating oils sold in the Middle Western States of U.S.A., by ten

[21] *Mech. Eng.*, 1931, **53**, 832; *J. Inst. Petr. Techn.*, 1932, **18**, 12A.
[22] *Oil & Gas J.*, 1932, **30** (52), 18; *J.S.A.E.*, 1932, **30** (5), 25; *Petr. Eng.*, 1932, **3** (6), 23; *J. Inst. Petr. Techn.*, 1932, **18**, 307A.
[23] *Petr. Eng.*, July, 1932, **3** (11), 32; *J. Inst. Petr. Techn.*, 1932, **18**, 384A.
[24] *J.S.A.E.*, 1932, **30**, 49.
[25] *Oil & Gas J.*, 31.3.32, **30** (46), 98; *J. Inst. Petr. Techn.*, 1932, **18**, 215A.
[26] *Oil & Gas J.*, 22.9.32, **31** (18), 12; *J. Inst. Petr. Techn.*, 1932, **18**, 431A.

of the major companies as grade S. A. E., No. 40, during the four years, 1929–1932, have been carried out and the results shown in a series of tables. The use of aluminium soap greases in the lubrication of rocker arms has been discussed by E. W. Zublin.[27]

Several papers of general interest on the subject of lubricating oils and lubricants have appeared recently. At the Lubrication Conference at Strasbourg in July, 1931, several important papers were read, including one on new equations for conversion of readings of several types of viscometers to kinematic viscosities. These papers have been reviewed by A. Graetz.[28] The viscosity-index and lubricating problems have been reviewed by G. H. Davis, M. Lapeyrouse and E. W. Dean[29] in a paper that contains a compilation of the more useful data and charts on viscosity-index. The original basis for the classification of lubricating oils according to viscosity-index is reviewed. In order to classify lubricating oils according to their viscous stability or rate of change of viscosity with change of temperature, a scheme, alternative to the Dean and Davis and D. P. Barnard systems, has been given by C. M. Larson and W. C. Schwaderer.[30] The use of the gravity-index in describing lubricating oils has been put forward by W. B. McCluer and M. R. Fenske,[30a] and the relationship between molecular fractions and absolute viscosities of blended lubricating oils has been examined by E. P. Epperson and H. L. Dunlap.[31] G. Wade and A. L. Foster[31a] have carried out an interesting series of experiments on the relationship between volatility and consumption of lubricating oils used in engines, and several conclusions have been stated.

In a study of low viscosity oils for motor lubrication, C. T. Doman[32] has described tests carried out to show the relation of oil viscosity to oil temperature and to power output, and of oil temperature to engine load. Further tests on the evaluation of lubricating oils by the work factor method have been given by K. O. Muller.[33] G. Bandte[34] has described researches on the relation between chemical constitution of the oil and its tendency to form carbon in engines. He concludes that, for oils with equal

[27] *Ind. Eng. Chem.*, 1931, **23**, 1434; *J. Inst. Petr. Techn.*, 1932, **18**, 52A.
[28] *J. Inst. Petr. Techn.*, 1932, **18**, 135.
[29] *Oil & Gas J.*, 31.3.32 **30** (46) 92; *J. Inst. Petr. Techn.* 1932, **18**, 212A.
[30] *Nat. Petr. News.*, 13.1.32, **24** (2), 26; *J. Inst. Petr. Techn.*, 1932, **18**, 123A.
[30a] *Ind. Eng. Chem.*, 1932, **24**, 1371.
[31] *Ind. Eng. Chem.*, 1932, **24**, 1369.
[31a] *U.S. Bur. Mines Tech. Paper*, 500, 1931; *J. Inst. Petr. Techn.*, 1932, **18**, 123A.
[32] *Oil & Gas J.*, 31.3.32, **30** (46), 95; *J. Inst. Petr. Techn.*, 1932, **18**, 213A.
[33] *Erdöl u. Teer*, 1932, **8**, 139, 156; *J. Inst. Petr. Techn.*, 1932, **18**, 166A.
[34] *Erdöl u. Teer*, 1932, **8**, 10; *J. Inst. Petr. Techn.*, 1932, **18**, 124A.

carbon-forming tendencies, the oil with the higher viscosity must have the lower viscosity-index; and, for oils of equal viscosity, the carbon-formation will be greater as the viscosity-index increases.

An interesting discovery has been made by E. Graefe[35] in establishing the presence of nitro-compounds in used lubricating oils, chiefly from Diesel engines. He considers that these were formed either from the fuel or from the lubricating oil, by chemical reaction with air, during the combustion in the cylinder. In a paper on the property of oiliness, H. B. Batchelor[36] includes some hints on the operation of the Herschel machine, and, in a further paper on the effect of oxidation on lubricating oils, the same author[37] describes the effect of oxidation on refined lubricating oils from paraffin-base and mixed-base crude oils. The use of olive oil as a lubricant for automobiles has been the object of road tests by M. Boucher,[38] who claimed satisfactory performance, and discusses the effect of this new outlet for olive oil upon the industry in Italy. An account of the effect of electric current on vegetable oils in the formation of voltols has been given by E. A. Ullan.[39]

The reclamation of used lubricating oil is an increasingly popular subject. The nature of crank-case drainings from aero-engines has been described by J. C. Schillaber.[40] Dust is usually not present to the same extent as in used automobile oils, but in certain regions—*e.g.*, Texas—considerable quantities of dust can be present. The use of clay and filter pads and of coagulants, such as trisodium phosphate and sodium silicate, are mentioned.

A description of a semi-industrial plant, involving the separation of the non-emulsified water, heating, introduction of steam to remove water and light hydrocarbons, chemical treatment ($ZnCl_2$), and finally, earth treatment and filtration, has been given in a paper on the recovery of used oils by the Korach-Randaccio process.[41]

Some interesting features have appeared in the patent literature during the year, but the usual patent specification contains material of only slight novelty and variation compared with previous practice or knowledge.

Synthetic lubricants have been mentioned in several patents[42];

---

[35] *Petr. Zeit.*, 8.6.32, **28** (23); *Motorenbetrieb*, **5** (6), 5; *J. Inst. Petr. Techn.*, 1932, **18**, 384A.

[36] *Petr. Eng.*, June, 1932, **3** (10), 33; *J. Inst. Petr. Techn.*, 1932, **18**, 342A.

[37] *Petr. Eng.*, Aug., 1932, **3** (12), 28; *J. Inst. Petr. Techn.*, 1932, **18**, 384A.

[38] *Olii. Min.*, 1932, **12**, 105; *J. Inst. Petr. Techn.*, 1932, **18**, 343A.

[39] *Olii. Min.*, 1932, **12**, 97; *J. Inst. Petr. Techn.*, 1932, **18**, 344A.

[40] *Aviation*, 1931, **30**, 641; *J. Inst. Petr. Techn.*, 1932, **18**, 11A.

[41] *Giorn. Chim. Ind. Appl.*, 1932, **14**, 228; *J. Inst. Petr. Techn.*, 1932, **18**, 344A.

[42] E.P., 358,495; 362,465; 363,823; 363,846; 364,110; 372,763; U.S.P. 1,877,664; *J. Inst. Petr. Techn.*, 1932, **18**, 15A, 89A, 90A., 263A, 432A.

in one case, the catalyst, aluminium chloride with aluminium or zinc dust, is covered. The division of an oil by sulphur dioxide extraction into fractions, rich in hydrogen and poor in hydrogen, before treatment, is another feature.

In the refining of petroleum lubricating oils, an apparatus is described[43] for vacuum distillation of lubricating oils, enabling high vapour velocities to be used in the fractionating column. Other distillation systems are also given.[44]

Numerous minor variations in acid, alkali and earth treatment of lubricating oils have been stated.[45] A number of patents[46] have been issued on the refining of lubricating oils with liquid phenol. The oil and undiluted liquid phenol are passed, at a temperature below that at which the phenol becomes completely miscible with the oil, preferably in counter-current, through a series of agitators, and, after settling, the oil and phenol layers are separated before they pass to other agitators. A separated purified oil layer (which is later subjected to distillation to remove absorbed phenol) and a phenol layer are removed from the end agitators of the series. The use of phenol and methyl alcohol is referred to in one case. A similar process[47] to separate oil into paraffinic and naphthenic fractions involves extraction with either an aromatic acetate or an organic thiocyanate; another process utilises furfuryl alcohol.[48]

Several patents[49] cover methods for imparting a green fluorescence to lubricating oils; the addition of small quantities of fractions obtained from coal tar, aluminium chloride-treatment residues, and asphaltene-like polymerisation bodies from spent Fuller's earth, are quoted for this purpose. Aluminium chloride treatment is mentioned in a process for the production of lubricating oils from cracked residues[50], and the use of additions of coal tar pitch and an adsorbent is referred to in a process for lowering the

---

[43] U.S.P. 1,877,987; cf. E.P. 381,427; *J. Inst. Petr. Techn.*, 1932, **18**, 432A, 466A.

[44] U.S.P. 1,860,838; 1,873,734; 1,879,948; 1,882,606; *J. Inst. Petr. Techn.*, 1932, **18**, 308A, 385A, 432A, 466A.

[45] U.S.P. 1,827,165; 1,831,265; 1,833,396; 1,836,947; 1,847,442; 1,847,623; 1,847,778; 1,849,653–4; 1,855,203; 1,856,141; 1,856,934; 1,859,514; 1,861,711; 1,881,044; E.P. 369,975; *J. Inst. Petr. Techn.*, 1932, **18**, 15A, 54A, 55A, 216A, 263A, 308A, 346A, 466A, 262A.

[46] E.P. 362,600; 369,737; cf. U.S.P. 1,860,823; 1,877,614; 1,878,022; *J. Inst. Petr. Techn.*, 1932, **18**, 89A, 216A, 308A, 432A.

[47] U.S.P. 1,874,946–7; *J. Inst. Petr. Techn.*, 1932, **18**, 385A.

[48] U.S.P. 1,883,374; *J. Inst. Petr. Techn.*, 1932, **18**, 466A.

[49] U.S.P. 1,839,012; 1,842,856; 1,868,473; 1,869,608; *J. Inst. Petr. Techn.*, 1932, **18**, 90A, 91A, 385A.

[50] U.S.P. 1,832,629; 1,850,869; 1,878,262; *J. Inst. Petr. Techn.*, 1932, **18**, 54A, 216A, 432A.

cold test of lubricating oils.[51] The use of a liquid alkali metal[52] for treating an oil in counter-current is a new departure in refining. Vapour-phase refining of lubricating oils is described in a process for decolorisation of distillates[53] and the use of brucite[54] or magnesium oxide or hydroxide is suggested for the removal of acidity from oils.

Hydrogenation is described as a method of refining lubricating oils[55] and the preparation of white oils.[56] On the subject of de-waxing,[57] some new ideas have been put forward such as: the use of methyl chloride or ethyl chloride as solvents, and the cooling of the oil by vaporisation of the solvent.

Among the patents of a general nature, the following have been described: lubricants and brake impregnating materials;[58] the use of mercury compounds[59] (other than the cyanide) to prevent acidification of fatty oils; the use of copper oleate[60] in a compound oil to vary its thermal conductivity; the cleaning of surfaces coated with lubricating oil sludge[61]; and the production of petrol-and-water-resisting greases.[62] Small quantities of polymerised styrene or indene, etc., have been put forward as stabilising agents in lubricating oil.[63] Other anti-oxidants that have been mentioned are hydrogenated glyoxalines, free from strongly negative groups.[64] Stabilisation of lubricating oils against oxidation is claimed[65] by treatment with colloidal bentonite at 500–850° F. under pressure and in contact with air or oxygen. The addition of small quantities of fatty acid soaps of dicyanodiamide, guanidine, etc., is claimed[66] to improve the wetting properties of a lubricant.

Pre-diluted lubricating oils are described[67] as being prepared by mixing a pressed paraffin-base oil and heavy naphtha, and cooling;

---

[51] U.S.P. 1,859,692; *J. Inst. Petr. Techn.*, 1932, **18**, 308A.
[52] U.S.P. 1,865,235; *J. Inst. Petr. Techn.*, 1932, **18**, 348A.
[53] U.S.P. 1,839,388; *J. Inst. Petr. Techn.*, 1932, **18**, 90A.
[54] E.P. 369,412; *J. Inst. Petr. Techn.*, 1932, **18**, 215A.
[55] E.P. 360,201; cf. 360,830; *J. Inst. Petr. Techn.*, 1932, **18**, 53A.
[56] U.S.P. 1,851,580; *J. Inst. Petr. Techn.*, 1932, **18**, 216A.
[57] E.P. 373,538; U.S.P. 1,862,874; 1,867,580; 1,871,172; *J. Inst. Petr. Techn.*, 1932, **18**, 308A, 346A, 385A.
[58] E.P. 359,602; *J. Inst. Petr. Techn.*, 1932, **18**, 15A.
[59] E.P. 368,025; *J. Inst. Petr. Techn.*, 1932, **18**, 169A.
[60] E.P. 371,643; *J. Inst. Petr. Techn.*, 1932, **18**, 263A.
[61] E.P. 375,724; *J. Inst. Petr. Techn.*, 1932, **18**, 346A.
[62] E.P. 376,310; *J. Inst. Petr. Techn.*, 1932, **18**, 346A.
[63] E.P. 379,717; *J. Inst. Petr. Techn.*, 1932, **18**, 431A.
[64] U.S.P. 1,805,953–4.
[65] U.S.P. 1,884,587; *J. Inst. Petr. Techn.*, 1932, **18**, 466A.
[66] U.S.P. 1,830,970.
[67] U.S.P. 1,831,053; E.P. 369,197; *J. Inst. Petr. Techn.*, 1932, **18**, 53A, 215A.

the wax is removed and the product blended with filtered cylinder stock and low-cold-test naphthenic-base oil. The use of a non-inflammable diluent, such as carbon tetrachloride, for this purpose, has been covered previously.[68]

A large number of patents[69] refer to processes for reclaiming contaminated oils involving, usually, heating with or without vacuum, filtration or centrifuging and, possibly, some chemical refining. It has been claimed that impurities in used lubricating oils can be coagulated by the addition of not less than 0.1 per cent. of triethanolamine.[70] The use of exhaust gases in an engine to vaporise light constituents in used oils has been mentioned,[71] and one process covers the special case of the removal of phosphorus from oils.[72]

DEPARTMENT OF OIL ENGINEERING AND REFINING
UNIVERSITY OF BIRMINGHAM.

[68] U.S.P. 1,796,857.

[69] U.S.P. 1,828,428–30; 1,831,094; 1,831,875–6; 1,834,654; 1,838,718; 1,842,983; 1,848,124–5; 1,851,432; 1,852,350; 1,855,685; 1,857,461; 1,869,008; 1,871,682; 1,872,963; 1,876,035; E.P. 366,071; 371,484; *J. Inst. Petr. Techn.*, 1932, **18**, 16A, 53–55A, 91A, 216A, 263A, 308A, 385A, 432A, 124A, 263A.

[70] U.S.P. 1,882,002; *cf. Inst. Petr. Techn.*, 1932, **18**, 466A.

[71] E.P. 363,852. *cf.* U.S.P. 1,866,970; E.P. 371,131; *J. Inst. Petr. Techn.*, 1932, **18**, 90A, 385A, 263A.

[72] U.S.P. 1,841,754; *J. Inst. Petr. Techn.*, 1932, **18**, 91A.

Gas Oil, Diesel Fuel Oil, and Fuel Oil.

By F. H. Garner, Ph.D., M.Sc., F.I.C. (Member).

Increasing attention is being given to the utilisation of the heavy fractions of petroleum, and particularly as to the employment of such products as fuel in compression-ignition engines. During the past year special attention has been devoted to the rating of Diesel fuels in respect of their ignition qualities.

Gas Oil.

The recovery of benzole from coal gas has increased during the past year, and a number of papers have appeared on the use of gas oil for this particular purpose. In a paper by F. White and S. Kellet,[1] the chief cause of the thickening or sludging of gas oils is stated to be the absorption of high boiling tar compounds of high sulphur content. Sulphuretted hydrogen and air or oxygen, either alone or in the presence of steam, did not cause sludging. These authors arrive at the conclusion that in order to minimise the trouble a low gas temperature to the scrubbers is essential. The oil in circulation is maintained in a clean condition by the use of a sludge tank and coke filter, and it is stated that the yield of benzole per ton was higher with gas oil than with creosote oil. Meurisse[2] deals with the ageing of absorption oils used for washing coke oven gas, and states that this is due to the formation of free carbon and asphaltic polymerised products. Free sulphur and sulphuretted hydrogen have no effect on the polymerisation which is, however, greatly accelerated by the presence of water. On the other hand,[3] it is claimed that the removal of sulphuretted hydrogen prior to the removal of benzene prevents the thickening of wash oils. It is stated that other factors causing thickening are the absorption of tar fog, the use of oil containing tar acids, and the removal of low boiling fractions from wash oil. Holmes[4] puts forward a new method for the evaluation of gas oils for use in carburetting water gas based on three factors, namely, specific gravity, dispersion (difference in refractive indices at 100° F. for C. and F. lines) and average boiling points. This work was based on the results obtained in small scale carburetting tests of various gas oils. Reference is also made to this method in a paper of the Proceedings of the American Gas Association,[5] and from another paper by O'Keefe,[6] in the

[1] *Gas World*, 1932, **96** (2496), Coking Section, 68–75.
[2] *Chimie et Industrie*, Special Number, 1932, March, 249.
[3] *Gas World*, 1931, **95**, Coking Section, 116.
[4] *Ind. Eng. Chem.*, 1932, **24**, 325; *J. Inst. Petr. Techn.*, 1932, **18**, 171A.
[5] *Am. Gas Assoc. Proc.*, 1931, **13**, 974.
[6] *Am. Gas Assoc. Proc.*, 1931, **13**, 1146.

same journal, it would appear from the results of experimental work in several laboratories that standardisation is needed of both the cracking apparatus and the method of procedure used in the determination of the carburetting qualities of gas oil.

The second report on the back-run process for the manufacture of carburetted water-gas has been issued by the Institute of Gas Engineers.[7] It is shown that the introduction of back-run steaming leads to a reduction in the amount of coke consumed, or an increase in the volume of gas made per day, or both. A gas with a calorific value up to 450–460 B.Th.U. was made without any appreciable loss in the efficiency of oil cracking.

Reference is also made to the use of heavy oil in water-gas plants,[8, 9] and the requirements for the heavy fuel oil are outlined. It is, however, pointed out that only a run on a semi-commercial scale will enable suitable oils to be selected. The method of operation requires the use of the checkerless carburettor fitted with an atomising spray, with some fuel oil vaporised directly on the fuel bed. The tars formed are in general more viscous than those produced from gas oil.

During the year a number of papers have appeared on the formation of resinous deposits from carburetted water-gas, coal and coke oven gas.[10] G. Berkhoff[11] ascribes the formation of these deposits largely to the reaction between nitrogen oxides and certain types of unsaturated compounds. When poor wash oil is used, it is considered that an increase in nitric oxide content of the gas takes place due to the evolution of this gas from the recirculated oil, which has previously been well saturated with nitrogen compounds. Ward, Jordan and Fulweiler[12] distinguish two types of gum found in gas distribution systems: (*a*) liquid-phase gum of low nitrogen content, which is said to be found only in carburetted water gas or mixed gas, and (*b*) vapour-phase gum, which is strongly acid and contains 5 per cent. or more of nitrogen. This type of gum is formed in the vapour-phase and accelerated by the presence of oxides of nitrogen, and is probably present in coal and coke oven gas.

Diesel Fuel Oils.

A number of important papers have appeared on the question of Diesel fuel oils during 1932, in view of the rapid development

[7] *Inst. Gas Engrs.*, 1932, Copyright Pub. No. 58; *Gas World*, 1932, **97**, 393 and 493.
[8] *Nat. Petr. News*, 8.6.32, **24** (23), 43; *J. Inst. Petr. Techn.*, 1932, **18**, 309A.
[9] *Am. Gas Assoc. Proc.*, 1931, **13**, 1150 and 1159.
[10] *Het. Gas*, 1931, **51**, 460 (Chem. Abstr., 1932, **26**, 1755).
[11] *Het. Gas*, 1932, **52**, 119 (Chem. Abstr., 1932, **26**, 6099).
[12] *Ind. Eng. Chem.*, 1932, **24**, 969; *J. Inst. Petr. Techn.*, 1932, **18**, 378A.

now taking place in high-speed Diesel engines for road work. At a Symposium of the Institution of Petroleum Technologists,[13] a number of papers were presented on the determination of the spontaneous ignition temperatures of fuels, and a comparison was made with starting and ignition delay tests in Diesel engines. A new type of apparatus developed at the Royal Aircraft Establishment was described by Foord, in which the relative ignition time lag can be measured. A review of recent German work on the measurement of spontaneous ignition temperatures was given by J. L. Chaloner. Le Mesurier gave a comparison of spontaneous ignition temperatures determined by both the Moore and Royal Aircraft Establishment apparatus with engine starting tests made in a McLaren-Benz engine, and also with several other engines, for the determination of ignition delay angle. It was stated that the correlation of the Moore test with the engine test was much less close than with the new apparatus of the Royal Aircraft Establishment. The results with the latter apparatus compare very favourably with the ease of starting determination on the engine, but cannot be compared with the delay angle under running conditions in all cases. An inertia lag meter for the measurement of ignition delay angle in Diesel engines was described by Broeze. In another paper[14] Boerlage and Broeze gave fuller details of the determination of ignition quality of Diesel fuels expressed in "Cetene Numbers," using cetene and α-methyl-naphthalene as reference fuels, in the same way as iso-octane and normal heptane in the determination of the knock ratings of gasolines. It is stated that physical characteristics such as viscosity, surface tension and specific gravity can be disregarded to a great extent in so far as ignition characteristics are concerned. For the determination of Cetene Numbers a 20 h.-p. Thomassen Delft engine was used, and an optical or pencil indicator was employed for the determination of the commencement of rapid pressure rise. A series of diagrams was made with varying throttle openings, and it was shown that the commencement of ignition (sudden pressure rise) gave a steady curve of hyperbolic character called the "Delay Curve." In the routine testing of fuels the difference in delay angle at two pressures, 15 and 30 atmospheres, is observed, and the results are expressed in terms of reference fuel, so as to give each fuel a Cetene Number. Naturally, sub-standard fuels are used in ordinary testing work instead of cetene and α-methyl-naphthalene. Mention is made of the hot-bulb engine, and it is stated that in some cases ignition is caused by fuel left over from the previous injection. It is pointed out that ignition quality in

[13] *J. Inst. Petr. Techn.*, 1932, **18**, 533–594.
[14] *J.S.A.E.*, 1932, **31**, 283, 338; *J. Inst. Petr. Techn.*, 1932, **18**, 346A.

Diesel engines is not all important, and that other factors of great importance are cylinder wear and complete combustion at high power. Attention is also directed to the factors involved in direct injection and pre-combustion in separate chambers, and suggestions are made to designers in order to ensure a degree of insensitiveness to the ignition qualities of the fuel used.

Pope and Murdock[15] have utilised a modified C.F.R. engine for the rating of Diesel engine fuels, which is based on the critical compression ratio for audible combustion. The critical combustion ratio is the mean of the two ratios obtained by lowering the compression ratio until firing ceases, and then raising the compression ratio with the engine being motored by means of a synchronous motor until firing again occurs. The paper is an account of preliminary work, but indicates that the C.F.R. engine can be used for the rating of Diesel fuels. Boerlage and Broeze (*loc. cit.*) consider that the measurement of the delay angle is preferable to the measurement of the firing limit as proposed by these authors. The factors which determine the duration of the delay period are discussed in the light of experimental results on a series of engines by Le Mesurier and Stansfield.[16] It is concluded that progress in Diesel engine design, in so far as it refers to combustion, depends on the use of the highest practical compression pressure and temperature at the moment of fuel injection. Neither flash point nor distillation range of a fuel are of importance in so far as the delay period is concerned in the case of Diesel engines, although in the case of certain small high-speed engines, fuels of high volatility may help to reduce the amount of exhaust smoke at low speed. Dicksee,[17] in a paper on problems connected with high-speed compression ignition engine development, investigated the behaviour of some 16 types of fuel. The spontaneous ignition temperature was determined in a simple type of the Royal Aircraft Establishment apparatus, and the relative suitability of the fuels was determined by engine tests in which a "Farnboro" indicator was used to measure the pressure rise. This author considers that it is the relationship between distillation range and ignition point of the oil which determines its suitability or otherwise as engine fuel. The vaporisation of the fuel is a very important factor in determining the knock, although possibly it is not the only cause. It is not considered that too volatile a fuel is satisfactory nor, on the other hand, one with too high a percentage of residue. Dunkerly[18] described an electrically-

[15] *J.S.A.E.*, 1932, **30**, 136; *J. Inst. Petr. Techn.*, 1932, **18**, 170A.
[16] *North-East Coast Inst., Engrs. & Shipbuilders*, February 26, 1932; *J. Inst. Petr. Techn.*, 1932, **18**, 328A.
[17] *Proc. Inst. Aut. Eng.*, 1931–32, **26**, 309.
[18] *Petroleum Times*, 1931, **25**, 389; *J. Inst. Petr. Techn.*, 1931, **17**, 244A.

heated silica tube furnace for the determination of spontaneous ignition temperatures of oil. Fractional distillation is also stated by Pyhälä[19] to be of great value in determining the suitability of Diesel fuel oils. He treats the oil in normal benzine solution with sulphuric acid, and distils to 250° C., 250–300° C. and 300–350° C., and claims that the lowest fraction should be at least 50 per cent. of the total, and the total of the two lower fractions at least 80 per cent. of the total, for the oil to be of good quality. In a publication of the National Advisory Committee for Aeronautics, No. 401 (1931), Rothrock has shown that by increasing the air temperature during injection the commencement of the combustion can be forced to take place during ignition, and so prevent the occurrence of detonation. The rate of fuel injection does not in itself control the rate of combustion. Equations for the kinetics of the chemical reactions, at the air-fuel inter-faces, which precede ignition in Diesel engines are derived by K. Neumann,[20] and it is calculated that the heat of reaction reduces the ignition delay by two-thirds. L. R. Underwood[21] describes experiments in which the flame in the combustion space of a compression-ignition engine is observed stroboscopically and photographed through a quartz window Results are shown of the effect of engine lag on ignition delay and duration of combustion. Practical difficulties present with certain differences in the physical properties of heavy fuels, in so far as engine designers are concerned, are discussed in the Sulzer Technical Review.[22] The principal drawbacks mentioned are high asphalt content and the presence of abrasive material in the fuel. It was shown that after 1000 hours service gas oil gave less than one-fifth the wear in cylinder liners that was experienced when a certain type of boiler fuel was used.

Coal tar has been investigated as a fuel for Diesel engines by Gautier,[23] who found that a number of modifications were required, including a very high compression ratio. The starting qualities were poor and in general the performance was much less flexible than with gas oil.

It is claimed that Diesel oils of which the ignition qualities are unsatisfactory can be improved by the addition of not more than 30 per cent. of the constituents of a Diesel oil which are insoluble

[19] *Teknillinen Aikakauslehti*, 1931, **21**, 141 (Chem. Abstr., 1932, **26**, 3098).
[20] *Z. Ver. deut. Ing.*, 1932, **76**, 765.
[21] *Inst. Mech. Eng.*, November 30, 1931; *J. Inst. Petr. Techn.*, 1932, **18**, 329A.
[22] *Sulzer Technical Review*, 1932, (3), 1; *J. Inst. Petr. Techn.*, 1932, **18**, 467A.
[23] *Rev. Comb. Liq.*, 1932, **10**, 1; *J. Inst. Petr. Techn.*, 1932, **18**, 264A.

in liquid sulphur dioxide.[24] The addition of a primer to fuel oil in order to shorten the delay period has been protected by E.P. 294,129, and it is now proposed[25] to introduce the primer with the air so that the fuel can be injected into an inflammable medium inside the cylinder. The amount of the primer so introduced can be controlled, and thus economy effected by limiting its use to those occasions when it will be most effective. The addition of a small percentage of an alkyl nitrate containing 2–4 carbon atoms in the molecule (as, for example, ethyl nitrate) to heavy fuel oil or creosote oil is stated to give an improved Diesel fuel oil.[26]

The use of Diesel oils for aviation engines in comparison with gasoline is discussed by Marcotte,[27] who also describes a series of various types of heavy oil motors. A suggested specification of Diesel fuel for aviation purposes is given by two Russian authors,[28] in which the pour point is limited to below −35° C., distillation range 175–350° C., and in addition limitations on sulphur, acidity, ash, flash point and copper dish test are suggested.

Detailed fuel consumptions of a fleet of 12 Diesel-engined tankers before and after fitting exhaust-heated boilers are given by Dilworth[29] showing an economy of 30 per cent. in auxiliary fuel consumption. An account of the experimental work carried out by the London General Omnibus Company since 1929 is given in the Journal of the Institution,[30] with particular reference to Junkers, A.E.C.-Arco, A.E.C.-Ricardo and Gardner 5-L.W. engines. A tentative specification for fuel is given, but it was felt that the stage had not yet been reached where a firm specification could be given. Fuels from coal tar were tried, but the results in every case were most disappointing. The general experience has shown that there is a definite future for high-speed compression-ignition engines for omnibus operations.

Fuel Oils.

A paper by Brame[31] drew attention to recent work on colloidal or coal-oil fuel. A summary of the information at present available was given, particular attention being drawn to the importance

[24] Edeleanu G.m.b.H., E.P. 381,941 (10.10.32); *J. Inst. Petr. Techn.*, 1932, **18**, 467A.
[25] Helmore, E.P. 366,947 (3.2.32); *J. Inst. Petr. Techn.*, 1932, **18**, 192A.
[26] D. T. Jones and I.C.I., Ltd., E.P. 374,481 (13.6.32); *J. Inst. Petr. Techn.*, 1932, **18**, 310A.
[27] *Rev. Comb. Liq.*, 1932, **10** (96), 201; *J. Inst. Petr. Techn.*, 1932, **18**, 409A.
[28] Tilicheev and Doladugin, *Neftyanoe Khozyaistvo*, 1932, **23**, 27 (Chem. Abstr., 1932, **26**, 5741).
[29] *Mar. Eng.*, 1932, **55**, 149; *J. Inst. Petr. Techn.*, 1932, **18**, 171A.
[30] *J. Inst. Petr. Techn.*, 1932, **18**, 866.
[31] *J.S.C.I.*, 1932, **51**, 855, 879; *J. Inst. Petr. Techn.*, 1932, **18**, 432A.

of the coal-oil mixture being permanently stable, as otherwise the risk of deposits forming in tanks and pipelines is always present. It is considered that the use of coal-oil fuels ashore is unlikely, and that the extended use of such mixtures for steam raising on board ship is at any rate many years ahead. Reference was also made to the recent trial in the steamship *Scythia* of a mixture containing 60 per cent. oil and 40 per cent. coal. In the discussion of this paper it was stated that no stabilisers were used in the *Scythia* fuel, but it was probable that the fuel oil used was a heavy residue obtained after cracking and had a high asphalt content. The possibilities of coal-oil fuels are further discussed in a paper by Strevens[32] from the point of view of power production by burning under boilers, in Diesel engines, and for the purposes of heat treatment giving oil products as distillates and smokeless fuels as residues.

An investigation of oil firing in the porcelain industry at an experimental station at Kyoto, Japan, is described,[33] and it was found that oil presented advantages over coal of more uniform heating, smokeless firing and greater economy than coal, not only from a cost point of view, but also as regards time and space required. The various factors in considering fuel for merchant ships are discussed by J. Johnson,[34] who gives diagrams and tables to show the relative merits of motor- and steam-driven ships as regards weight, space, and initial and running costs. He considers the position of steam propulsion is a strong one in so far as fuel costs are concerned. A study of coal and fuel-oil costs of a plant fitted with 25,000 K.W. turbo-alternators showed maximum overall thermal efficiency based on the total kilowatt-hours generated at economic load was 26·95 from coal and 27·65 from oil firing.[35] A general review of the increased utilisation of fuel oil in France is given by A. Minne,[36] who also gives a classification of the various types of burners used. A second paper[37] reviews the types of burners used with liquid fuel for central heating and hot-water service in France.

Goodwin[38] has described the results obtained by a special process for the removal of heavy bottom settlings and solids found in most residual cracked fuels to a few tenths of 1 per cent. A

[32] *Fuel Economist*, 1932, **7**, 403.
[33] M. Akazuki, *J. Fuel Soc.*, Japan, 1931, **10**, 1007.
[34] *Engineering*, 1932, **133**, 340; *J. Inst. Petr. Techn.*, 1932, **18**, 170A.
[35] *Engineering*, 1932, **133**, 704; *J. Inst. Petr. Techn.*, 1932, **18**, 310A.
[36] Minne, *Rev. Comb. Liq.*, 1932, **10** (95), 157; *J. Inst. Petr. Techn.*, 1932, **18**, 348A.
[37] Altchidjian, *Ann. des Comb. Liq.*, 1932, **7**, 373; *J. Inst. Petr. Techn.*, 1932, **18**, 432A.
[38] *Nat. Petr. News*, 1931, **23** (29), 46.(30) 45; *Refiner*, 1932, **11**, 188 and 513.

commercial plant with a capacity of 2500 barrels per day was operated successfully for some time with charging stocks of varying characteristics. It is stated that this practice has a direct commercial application to the solution of many refinery problems, such as the production of a low-viscosity fuel oil by stabilising cracked residuum and the elimination of excess sediment and water. The use of this process permits the unrestricted use of lime to reduce corrosion in cracking equipment, since the lime-sulphur compounds so produced are removed along with the carbonaceous matter.

An interesting comparison of fuels is made by R. S. McBride,[39] who gives tables and diagrams to illustrate the trend in fuel and energy supplies in the United States for the last 70 years.

[39] *Chem. & Met. Eng.*, 1932, **39**, 184; *J. Inst. Petr. Techn.*, 1932, **18**, 217A.

Oil Engine Development.

By P. N. Everett, A.M.Inst.C.E.

I. General.

Development continues along the lines indicated in the last report. Air injection is disappearing and all new designs utilise airless injection of the fuel. Two-stroke cycle double-acting engines of various designs appear to have established themselves for the really large sizes, but the addition of supercharging will enable the 4-stroke cycle engine to compete with the 2-stroke cycle single-acting engine for all but the largest sizes.

In the case of the intermediate size engine, say 100 b.h.p. to 1000 b.h.p., there is a continual move to higher r.p.m. and a larger number of small cylinders, giving a smaller and lighter engine. Six-cylinder engines are now very common and there is a tendency to go to 8-cylinders.

It is getting more difficult to divide engines into groups according to the duty performed, as the same engine, with slight alteration to base plate, etc., is used as a stationary, marine and locomotive engine. With a view to lighter engines there has recently appeared on the market several engines with framework of steel parts welded together. Probably the Vickers submarine engine (although not welded) pioneered this design. The first practical welded design was the M.A.N. battleship engine, and this same construction has been used by them for quite small engines. In this country the Stevens' patent framework, as described in a paper to the Diesel Engine Users' Association by Mr. C. H. Stevens on October 12th, 1932, initiated several firms into this class of work. This design was primarily suggested for locomotive and high speed marine engines, but is now proposed for stationary land engines and any place where light weight is essential.

Engines of the lighter type have for some time been fitted with through bolts from crankshaft to cylinder, too, and this feature is now appearing in normal stationary engine design.

There is a general move to enclose all moving parts and fit a complete automatic lubricating system even to such parts as valve levers, etc. This is all to the good if accessibility is not sacrificed.

Aluminium alloy pistons have been in successful use in small size engines for some time, but there is little indication that they will be adopted generally in the larger sizes.

Piston ring design has received a good deal of attention recently, but there is a tendency to return to the plain Ramsbottom ring,

and more attention is being paid to the position of the rings in the piston and the method of fitting.

Modern design tends to a compromise between the old Diesel engine design with a camshaft at cylinder head level driven by vertical shaft and skew gears, and the old gas engine design, with a gear driven camshaft in the crankcase and long heavy push rods. Modern design has the camshaft midway, covered in but accessible, driven by gears or chain and valve levers operated by short light push rods.

There is a growing tendency amongst all builders to buy fuel pumps, and, to a lesser extent, fuel injectors from firms specialising in this class of work. The Bosch pump is becoming more and more in evidence, but many alternative designs are now available.

The automatic spring-loaded needle valve is the design of fuel injector fitted to almost every engine, and it has up to now given the best results in service, but some very good experimental work has been done on the open nozzle design by Dr. S. Berg and G. Rhode in Germany (*Automobile Engineer*, August, 1932).

It is worth recording that all oil engine development appears to assume that there is, and always will be, an unlimited amount of thin distillate fuel available, and very little consideration is being given to the problem of utilising residual fuels.

II. Stationary Engines.

Probably due to the bad times, the oil engine as a power producer is more than holding its own in relation to other power producers, and there is little doubt that when financial conditions improve, many large oil engines will be ordered. During this year a Sulzer double-acting, 2-stroke engine, having a normal loading of 11,400 b.h.p. at 136 r.p.m., has been ordered for the power station in the French Concession, Shanghai. When installed, this station will have a total of 42,600 b.h.p. in 9 engines, and will be the highest powered oil engine station in the world.

The shop trials have been completed of the largest oil engine yet built. This is the double-acting, 2-stroke, airless injection engine, built by Burmeister and Wain, Copenhagen. This engine develops 22,500 b.h.p. in 8 cylinders at 115 r.p.m., and is to be used for driving a dynamo at the Copenhagen Power Station. The piston is 840 mm. diameter and has a stroke of 1500 mm. This firm now say they are prepared to build this size cylinder in a 12-cylinder unit, giving 45,000 b.h.p. at 190 r.p.m.

Both 2- and 4-stroke cycle engines continue to be built, but for the medium size engine 300 b.h.p. to 1500 b.h.p., the 4-stroke airless direct injection engine appears to be the popular unit.

From 300 b.h.p. downward many different types of engine can be purchased, 2 or 4 stroke, horizontal or vertical, direct injection or prechamber.

In this field, also, the direct injection 4-stroke cycle engine predominates, but there are many good examples of 2-stroke cycle engines and also prechamber engines. Where high r.p.m. are not necessary, the horizontal engine still offers advantages and has a good market.

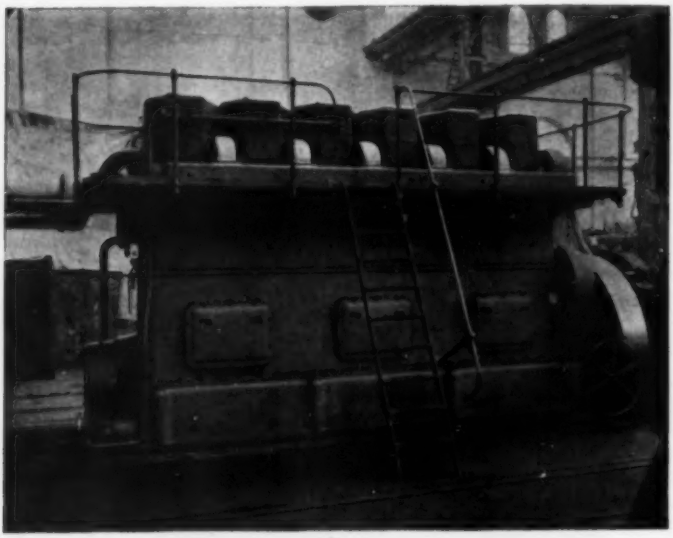


FIG. 1.

NATIONAL 4-CYCLE ENGINE, 630 B.H.P. AT 300 R.P.M.

The following descriptions are of some of the latest stationary type oil engines.

National Gas Engine Company, vertical 4-cycle engine, using direct airless injection, and developing 630 b.h.p. at 300 r.p.m. in 6 cylinders (Fig. 1). This engine has 15½ in. diameter cylinder and 18 in. stroke. Enclosure of the working parts has been done without interfering appreciably with accessibility. The camshaft is gear driven at about half-way up the engine. There are individual Bosch pumps with National Gas Engine injectors. The full load fuel consumption is given as 0·38 lb./b.h.p./hour.

Marshall, Sons and Co., Ltd., Gainsborough. Vertical, 4-cycle engine, using direct airless injection, and developing 80 b.h.p. at 750 r.p.m. in 2 cylinders (Figs. 2 and 3). This engine has 8½ in. diameter piston with 10 in. stroke. Enclosure is carried out to the fullest possible extent. The full load fuel consumption is given as 0·395 lb./b.h.p./hour.

FIG. 2.

MARSHALL 4-CYCLE ENGINE, 80 B.H.P. AT 750 R.P.M.

The Atlas Diesel Co., Stockholm. Vertical, 2-cycle engine, using direct airless injection and developing 435 b.h.p. at 250 r.p.m. in 3 cylinders (Fig. 4). This engine has 340 mm. diameter piston with 570 mm. stroke, and full load fuel consumption is given as 0·365 lb./b.h.p./hour. The engine has a reciprocating scavenge

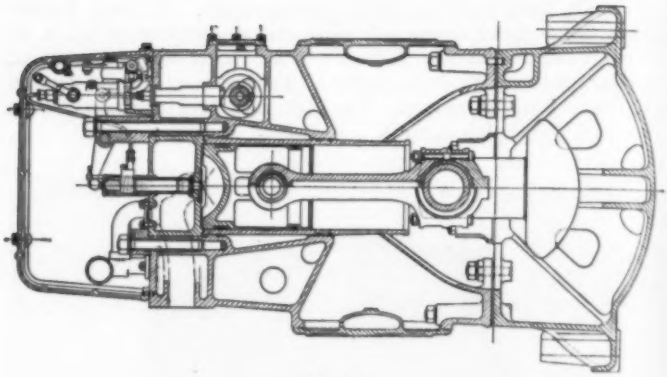


FIG. 3.
SECTION THROUGH MARSHALL 4-CYCLE ENGINE.

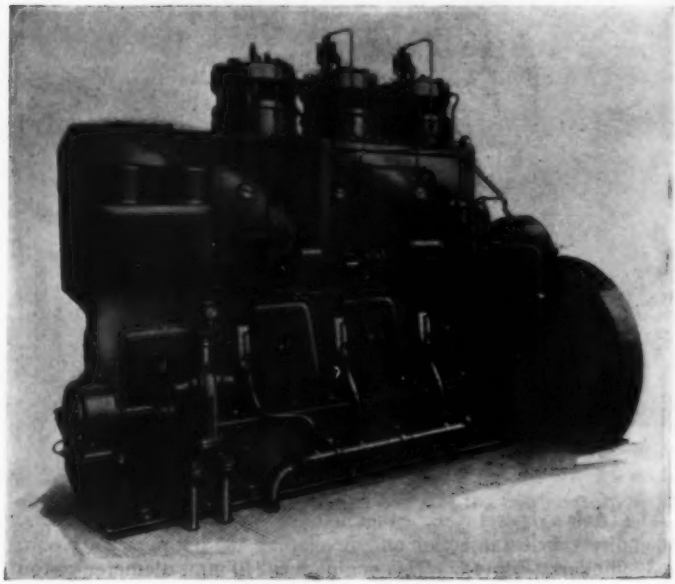


FIG. 4.
ATLAS DIESEL 2-CYCLE ENGINE, 435 B.H.P. AT 250 R.P.M.

pump driven from the crankshaft. An 8-cylinder engine of the same bore and stroke, developing 1400 b.h.p. at 300 r.p.m. has recently been supplied.

Amongst small sizes of 5 b.h.p., and even lower, the petrol-paraffin engine is being rapidly superseded by the high-compression

FIG. 5.

RUSSELL NEWBERY DIESEL ENGINE, 9 B.H.P. AT 1000 R.P.M.

engine using gas oil. Both horizontal and vertical designs are being produced, but vertical predominates, a good example being the engine built by Russell and Newbery, Altrincham (Figs. 5 and 6). This engine is also made in 2, 3, 4 and 6 cylinders.

III. Marine Engines.

The following large marine installations have been completed during the year.

The German Gunnery training ship "Bremse," twin-screw, totalling 26,000 s.h.p. in eight M.A.N. 2-stroke, airless injection, double-acting engines running at 600 r.p.m., bore 300 mm., stroke 440 mm. Four engines drive each shaft through gearing.

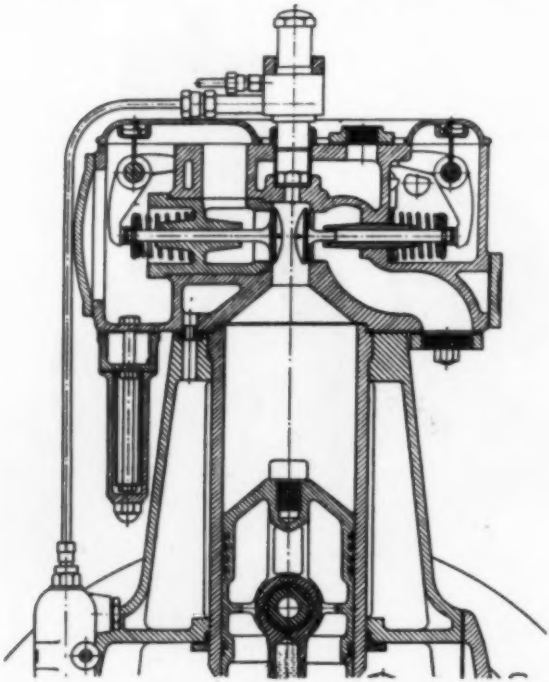


Fig. 6.

SECTION THROUGH RUSSELL NEWBERY ENGINE.

The Italian liner, "Neptunia," 4-screw, totalling 18,000 s.h.p., engines Sulzer type, 2-cycle, single-acting, running at 130 r.p.m. Air injection is used. Cylinder diameter 680 mm., stroke 1000 mm.

The White Star liner "Georgic," twin-screw, totalling 20,000 s.h.p. at 110 r.p.m., Harland and Wolff, 4-cycle double-acting engines, being very similar to the "Britannic" completed last year.

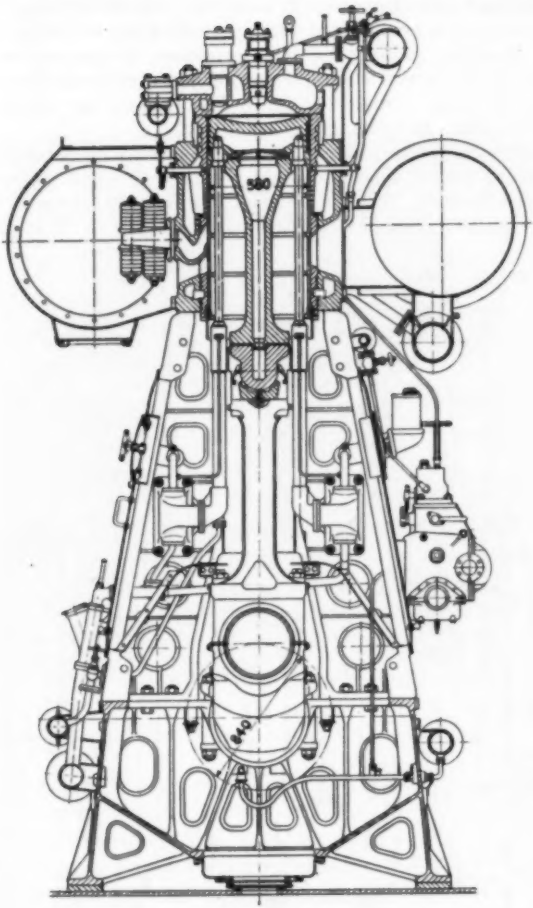


FIG. 7.

CROSS SECTION OF SULZER 8500 B.H.P. ENGINE.

Fast high powered cross-channel boats continue to be fitted with Diesel engines, a particular example being the "Prince Baudouin" now building for the Dover-Ostend service. It will develop a speed of 24 knots and is being fitted with specially designed Sulzer single-acting, 2-stroke, airless injection engines, developing a total of 17,000 s.h.p. in two shafts, direct driven at 268 r.p.m., bore of cylinder 580 mm., stroke 840 mm. The engines are building at John Cockerills, Belgium (Fig. 7).

As indicating the increase in power and speed with corresponding reduction in weight, mention might be made of a new engine built by Messrs. Sulzers. It is a 2-cycle, double-acting engine giving 6000 b.h.p. in 3 cylinders at 265 r.p.m. (Fig. 8). The cylinder

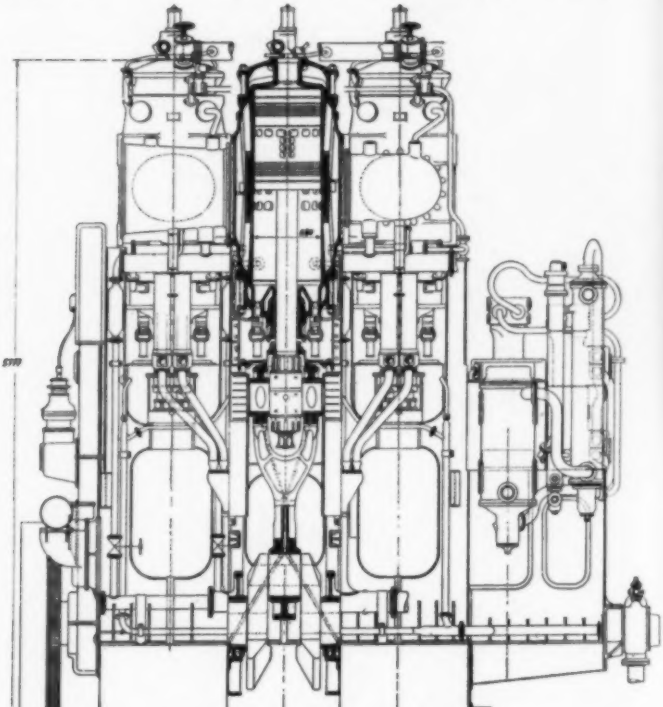


FIG. 8.

HIGH-SPEED DOUBLE-ACTING SULZER 2-CYCLE ENGINE OF 6400 B.H.P. AT 265 R.P.M.

diameter is only 680 mm. and the weight 24 lb. per b.h.p. This engine has run with both air and airless injection.

An engine of similar output and airless injection has been built by the M.A.N. Company, Germany.

If such an engine were built as a 12-cylinder unit, then a 4-screw boat could develop 100,000 s.h.p.

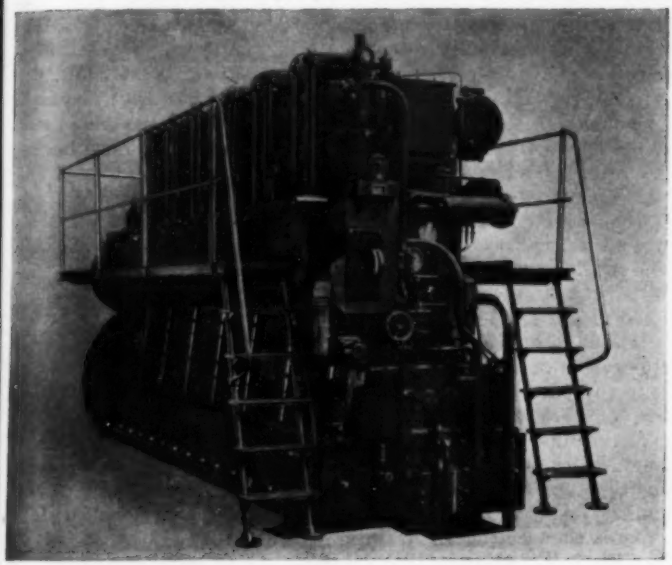


FIG. 9.

MAN 4-CYCLE ENGINE, 550 B.H.P. AT 270 R.P.M.

Supercharging in 4-cycle engines is gaining ground and the various designs can be classified under :—

Exhaust turbo charging.

Topping up system with rotary blower.

Pressure charging from underside piston.

These various systems are well analysed by Dr. Oppitz in the *Motorship* for April, 1932.

The Japanese are now designing and building their own engine, and the design is apparently based on all the various types they have built under licence during recent years.

Oil engine drive is very popular for small naval craft for coastal defence and such work, a good example being the two gunboats recently delivered to the Persian Government. These boats have twin-screws, a total of 2500 s.h.p. in Fiat 2-stroke engines, 6-cylinder, running at 330 r.p.m. Air injection is used.

There is a growing interest in the application of Diesel engines to trawlers, and several have been completed recently, but all for foreign owners. A particular example is the "Fismes," built to the order of Messrs. Rene Maubaillarcq by Smith's Dock Co. The main engine was built by the M.A.N. Co., and is a 4-cycle, airless injection 6-cylinder engine, developing 550 b.h.p. at 270 r.p.m. (Fig. 9). A separate auxiliary engine is fitted to drive the trawl winch, also an M.A.N. engine of 4 cylinders, 125 b.h.p. at 405 r.p.m. A smaller auxiliary set consists of a Gardner 3-cylinder engine, developing 20 b.h.p. at 700 r.p.m. driving a generator, air compressor and bilge pump.

For small river and harbour craft the small Diesel engine is rapidly superseding the petrol-paraffin engine once so popular for this duty. The smaller engines are very similar to those fitted to road vehicles.

IV. Engines for Locomotives.

It is in locomotive work where the greatest development in the application of the Diesel oil engine has taken place. Almost every railroad, both great and small throughout the world, is testing out some scheme involving the Diesel engine.

Many different drives are being utilised, small rail coaches, and small goods locomotives have clutch and gear box with propeller shaft to axle, like a motor car. The intermediate sizes have a similar drive or some simple electric drive. The most popular drive is the electric, but it apparently is also the most expensive. Various forms of hydraulic transmission are being tried out, and will probably be extensively used pending the time when the Diesel engine is developed sufficiently to couple direct.

An important event this year is the successful trials in service that have taken place on the London and North Eastern Railway of the Armstrong Sulzer Rail Coach mentioned in the last review. This coach has now been officially taken over by the Railway Company, and is in daily service. During its probationary period it covered over 20,000 miles during 20 weeks, and never failed to keep its time. On local work with a severe service, the consumption has averaged 5¼ miles to the gallon of fuel, and at rush periods as many as 120 passengers have been carried.

A 40 ton, 250 h.p. Diesel electric shunting locomotive by the same firm has been put into trial service by the London and North Eastern Railway.

During this year the German State Railways have put into regular service a Diesel electric rail coach on the Hamburg-Berlin route, it being the fastest train in Germany. The engine is a 12-cylinder Vee engine rated at 400 b.h.p. at 1400 r.p.m., built by the Maybach Co. The first engines have air injection of the fuel; later engines will have airless injection. With the trailer coach 150 passengers are carried normally. Many smaller Diesel rail coaches are in use in Germany, some with Maybach and some with Linke-Hofmann engines.

The Austrian State Railways are building several Diesel electric locomotives, some with Simmering engines of 160 b.h.p., being 4-cycle, airless injection, Vee type, and others with 300 b.h.p. Grazer engines, of the 4-cycle, airless injection vertical type.

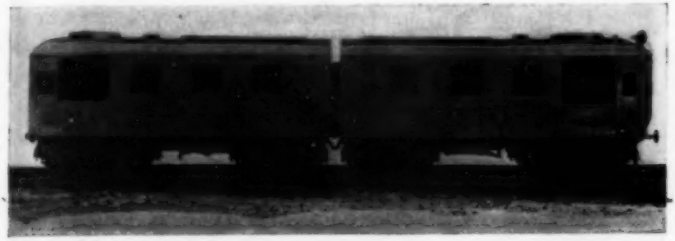


FIG. 10.

ARMSTRONG-SULZER 1700 B.H.P. DIESEL ELECTRIC LOCOMOTIVE.

During this year the three 1700 b.h.p. Diesel electric locomotives (mobile power houses) for the Buenos Ayres Great Southern Railway, South America, have been completed by Messrs. Armstrong Whitworth & Co., at their Scotswood Works, the engines having been built by Sulzers. Each locomotive draws 8 coaches, and these are the most powerful Diesel locomotives built in Europe (Fig. 10).

A good example of a small Diesel rail coach has been built by Messrs. Walker Bros., Wigan (Fig. 11), for the Clogher Valley Railway, North Ireland. Gear drive is used, and the engine is a Gardner 6-cylinder, developing 102 b.h.p. at 700 r.p.m., 4-cycle, airless injection.

Generally the development of the main line Diesel locomotive is only going slowly, but there is great activity in the Diesel rail coach, and for small contractor locomotives up to 60 b.h.p. very soon nothing but Diesel engine drive will be used.

V. Engines for Road Vehicles.

This development continues, but at the moment its further development is likely to depend as much, if not more, on political and economical features than on design.

In design there has been no startling development, but there has been a marked improvement in detail in the engines giving better running—quieter with less smoke, also improved lubricating oil consumption.

Fig. 11.

100 B.H.P. DIESEL RAIL COACH BY WALKER BROS.

There is now a very large number of different designs of engine on the road but they can be classified as follows :—

I. Direct injection with open chamber.: Gardner, M.A.N., Junker, Renault, Leyland, Petter, Michel, Beardmore.

II. Direct injection with separate chamber : Oberhansli, Linke-Hofmann, Ricardo as built by A.E.C., Dorman, Crossley.

III. Prechamber : Mercédès-Benz, Deutz, Bussing, Ganz.

IV. Expansion air cell : Saurer, M.W.M., Lanova, Cummins.

The makers of engines with the largest amount of actual road experience are Mercédès-Benz, Saurer, Gardner, Junker, M.A.N., Deutz, A.E.C., and it is interesting to note that this list includes engines of all four types mentioned above. It is impossible to say at present which type will eventually prevail.

As mentioned in the last report, the Diesel engine appears well established for the heavy commercial vehicle. During the year there has been a considerable extension in the application of the Diesel engine to bus work, but only for local runs and not for long distances. For this work higher powers are in some cases necessary, and larger engines up to 150 b.h.p. have been designed. A great many municipalities are running Diesel buses, and this looks like being an important application.

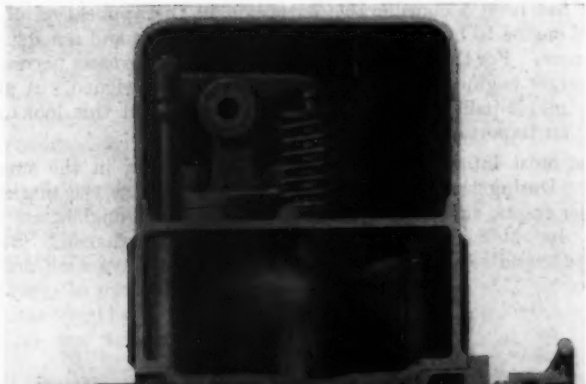
The most interesting development is, however, in the smaller sizes. During the year several firms have put on the market a smaller engine suitable for a 2–3 ton lorry. Such engines are now built by Mercédès-Benz, Deutz, Junker, Oberhansli, Saurer, Dorman, and several other firms are known to have such designs in hand. This opens up a very much larger sphere of operation for the Diesel engine. Of all types and sizes of Diesel lorry and 'bus there are now approximately the following numbers on the road :—

Great Britain	1500
Germany	1700
France	5500
Other countries, say	1300

It is too early to give definite information regarding maintenance, but all information to hand would indicate that the maintenance is not going to be much different from the petrol engine. A weak spot in most designs has been the crankpin bearing, but this difficulty appears to be decreasing.

Two interesting engines to report are those made by Henschel & Sohn, Kassel, Germany, and the Michel Motor Co., Kiel, Germany. The Henschel engine (Fig. 12) is made under licence from Lanova A.G., Munich, and is the expansion air cell type, but the arrangement of sprayer and air cell is entirely different from the Saurer. In the case of the Lanova, they are both arranged in a horizontal plane, and as the gases expand from the air cell they are given a circular motion by the form of the cylinder head, thus creating turbulence. The two air cells allow of a step down in pressure so that only about 40 atmospheres pressure exists in the cylinder. The 6-cylinder engine develops 110 b.h.p. at 1500 r.p.m. and weighs 770 kg.

The Michel engine is not so far manufactured by any firm on a production basis, but some very promising models have been made. Fig. 13 shows an engine giving 160 b.h.p. at 2000 r.p.m. The cylinder diameter is 67 mm. and stroke 116 mm. From a close study of the design it will be seen that this engine contains



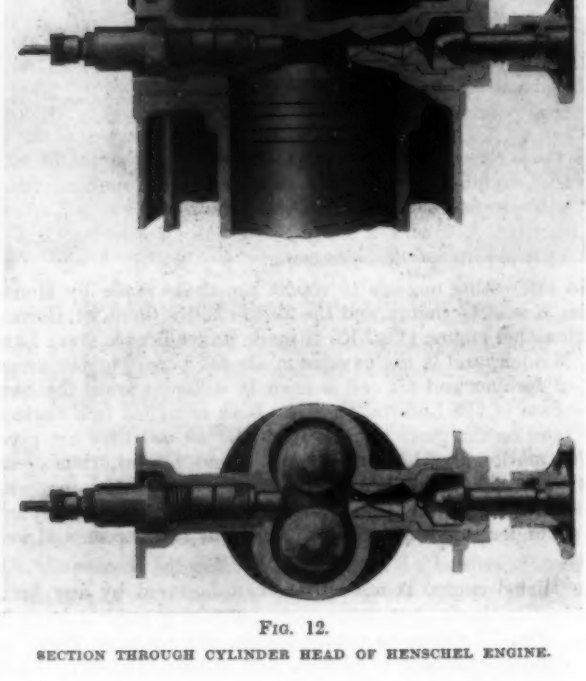


FIG. 12.

SECTION THROUGH CYLINDER HEAD OF HENSCHEL ENGINE.

many useful ideas. One of the most important is the ease with which it can be supercharged, giving figures for horse power per litre unheard of before. By special design and manufacture this firm claims to have overcome the difficulty of sticking piston rings. This interesting engine is described by Dr. Davis in *Engineering*, September 9th, 16th and 23rd, 1932.

Engineers are still working hard on the design of low compression engines to burn heavy fuel. They are of two main types. In the one there is a normal carburettor and an external vapouriser —of this type no design appears to withstand the severe duty of road service. In the other case the design arranges for the fuel to be injected by a Bosch or similar pump, and there is the equivalent of an internal vapouriser. Thus there is pump and injector as well as magneto and spark plug, and in some cases also carburettor and petrol fuel for starting up. The best known of this type of engine is the Hesselman, which is receiving much attention in many parts of the world. So far they are chiefly used for tractors and portable plants, and only a few are being tried out on the road.

VI. Engines for Aeroplanes and Airships.

It is very difficult to gather authorised information regarding the development of the Diesel aero engine. It is known that a good deal of pioneer work has been done in England, Germany and U.S.A., and also other countries. Something like fifteen firms are working on the problem, and there is little doubt that at some future date suitable Diesel engines will be available for this duty.

The difficulties experienced include the obtaining of a reasonable weight-power ratio, the equal distribution of fuel to all cylinders at all loads, good idling and, further, the characteristics of the Diesel are such that in service, in some cases, difficulty is being experienced in gliding.

The Packard Diesel engine is reported to be in daily use in U.S.A., and some of the Mid-European countries, but the only definitely known case where Diesel aeroplanes are in service is the freight carrying machines of the Luft Hansa flying between Berlin and Amsterdam, which are fitted with Junker Diesel engines.

In Germany it is reported that the Mercedes-Benz, Maybach and M.A.N., are engaged in the construction of engines for the new airship, in which case the weight-power ratio requirement is not so exacting.

A new engine produced in the U.S.A. is the Guiberson, which is a radial air-cooled 4-cycle engine with single valve, something like

the Packard. The engine made has 9 cylinders developing 185 b.h.p. at 1925 r.p.m., bore 4 13/16 in., stroke 6 in., weight 2·74 lb. per b.h.p.

It would appear that of all the types of engine available at the present time, the one most suitable for aircraft work is the 2-cycle direct injection, fitted with some superchanging arrangement. In this connection it is interesting to refer to the road vehicle section of this report, to the Michel engine.

This design is capable of producing an engine of about 2 lb. per b.h.p. at reasonable r.p.m. Very high mean pressures have been recorded on the experimental engine.

Asphalts and Road Materials

By W. W. Goulston, B.A., B.Sc., A.I.C. (Member).

General.

An indication of the general world position regarding the production of asphalt is shown by the production figures given for the U.S.A. by Prevost Hubbard in "The Mineral Industry During 1931" (published by the McGraw-Hill Book Company Inc. of New York). The total production of asphaltic materials in the U.S.A. during 1931 was 4,067,639 short tons, which is 2·1 per cent. less than the year before. The total sales of petroleum asphalt by refineries in the U.S.A. were 10·7 per cent. less in quantity and 28·2 per cent. lower in value. The quantity used for road work, paving grades together with road oils and cut-back asphalts, was 2,878,817 short tons, which is an increase of 7·4 per cent. over that used in 1930. It is interesting to note that there was a large increase in the use of road oils and cut-back asphalts. There was an actual increase of 36·8 per cent. in the use of these materials, whereas there was a reduction of 16·2 per cent. in the use of paving grades of asphalt. The increase in the use of road oils and cut-back asphalts shows the greater use of low cost bituminous types of surfacing, especially in the construction of secondary roads. In this connection it is of interest to note that the output of emulsified asphalt in the U.S.A. in 1931 was over one-third larger than in 1930.

Chemical.—The study of the composition of asphalt is attracting a good deal of attention. Various investigators have put forward suggestions which are summarised in a paper by Pöll,[1] who prefers to divide asphalt into oily constituent, oily resins, asphaltic resins, hard asphalt, carbenes and carboids. A contribution by Kalichevsky and Fulton[2] recommends separating the components of asphalt according to Marcusson's scheme into asphaltic acid, asphaltic anhydrides, asphaltenes, asphaltic resins and residual oil. They have examined the properties of these components, and trace their effect on the behaviour of asphalt in actual use. Baskin[3] also deals with the composition of asphalt according to Marcusson's classification, and draws attention to the fact that asphaltic acids and anhydrides are present in certain natural asphalts in quantities up to 12 per cent., but rarely show more than a trace in petroleum asphalts.

---

[1] *Asphalt u. Strassenbau*, 1932, **28** (8), 2–7.
[2] *Nat. Petr. News*, 21.12.31, 33–36; *J. Inst. Petr. Techn.*, 1932, **18**, 55A.
[3] *Oil & Gas J.*, 14.7.32, **8**, 36; *J. Inst. Petr. Techn.*, 1932, **18**, 349A.

There is a considerable divergence of opinion as to the desirability and effect of paraffin wax in asphalt. This subject is discussed by Longinus,[4] Manheimer[5] and Bandte,[6] the last of whom rightly points out that the value of asphalt for road-making and other purposes is not largely determined by the paraffin wax and sulphur content but depends on the chemical constitution of the asphalt as a whole.

The South Metropolitan Gas Company[7] has issued a second brochure on the measurement of the viscosity of coal tars and pitches. In this investigation Pickard shows that the viscosity-temperature relationship of tars is covered by the same general expression $CT^n a$ as was found for the consistency-temperature relationship when using the Metro trough viscometer. The relation between the various technical tar viscometers and a comparison of these instruments with absolute viscometers was studied by Pickard, who shows that at any one temperature all the technical instruments tested measure a function of the absolute viscosity.

An investigation of historical interest has been carried out by Spielmann[8] on the material used by the ancient Egyptians for embalming. By applying the test of fluorescence and by the spectroscopic analysis of the ash, he is able to prove that asphalt was used for this purpose mixed with wood-tar and resin.

Rock Asphalt and Natural Asphalt.

The production of Trinidad natural asphalt during 1932 was only about 50 per cent. of the production in 1931,[9] and the export of this material from Trinidad during this period showed a similar reduction. An interesting article on the operation of the Trinidad asphalt lake has appeared, in which the method of production and the application of the Trinidad lake natural asphalt is described.[10]

The efficient separation of asphalt from the Alberta tar sands has been a subject of long investigation. A successful method has now been found, and is described in a report issued by the Alberta Research Council.[11] The tar sand is mixed and heated with a solution of soda ash until all its acidity is neutralised and then washed with water. In actual plant operations 1 to 1½ lb. of alkali per ton of bituminous sand is used, and it is claimed that practically 100 per cent. of the bitumen content of the sand is recovered.

---

[4] *Erdöl u. Teer*, 1932, **8**, 125–127; *J. Inst. Petr. Techn.*, 1932, **18**, 172A.
[5] *Petr. Zeit.*, 30.4.32, **28** (16), 1–9; *J. Inst. Petr. Techn.*, 1932, **18**, 264A.
[6] *Erdöl u. Teer*, 1932, **8**, 380–383; *J. Inst. Petr. Techn.*, 1932, **18**, 386A.
[7] South Met. Gas Co., 1932.
[8] *J. Egypt. Arch.*, **18**, Pts. 3–4; *Nature*, 1933, **131**, 588.
[9] *Daily Oil Bull.*, 29.11.32.
[10] *Petr. Zeit.*, **28** (33), 2.
[11] *Petr. Times*, 29.10.32.

An interesting article has appeared on the German asphalt mines at Eschershausen.[12] The asphaltic limestone deposit contains 1–14 per cent. of bitumen and, for certain purposes, must be mixed with Trinidad épuré or petroleum asphalt to increase the bitumen content. The Eschershausen deposits are the only native source of natural asphalt in Germany at present available. The production is falling off owing to the increasing popularity of other types of bituminous road materials.

An extensive deposit of rock asphalt has been discovered near the Abu Derba oilfield in Sinai.[13] It is stated that half a million tons can be quarried, and much larger quantities may possibly be obtained by mining operations in the lower strata of the adjacent hills. The deposit appears to be a quartz sandstone impregnated with a hard and non-ductile bitumen. The extracted bitumen has a penetration of 7 and nil ductility. Technical experiments are in progress to determine the value of the material, but commercial exploitation is hindered by the absence of transport facilities.

Petroleum Bitumen.

Manufacture.—The types of crude oil necessary for the production of asphalt have been greatly extended. Baskin[3] in his paper, previously referred to, points out the fallacy of rigidly sub-dividing petroleum into asphalt and paraffin base crudes. He shows that predominantly "paraffin base" crudes can be processed to yield typically asphaltic residues, by distilling off the paraffinic portions and, if necessary, blowing the residue. The same opinion is expressed by Hausman,[14] who also describes the production of asphalt from the cracked residue of a flash type Dubbs unit.

The most recent advances in plant for the manufacture of asphalt are described by Glenn,[15] who gives a description of some plants recently erected in the U.S.A. One plant is designed to distil heavy crude oils in two stages, the crude being first distilled under atmospheric pressure in a tube still, and the residuum from the first stage is further distilled under vacuum in a second tube still. A second plant is also designed as a two-stage unit, but in this case there is only one tube still. The feed to the plant, which is either reduced crude or cracking stock residuum, passes through the entire convection section of the tube still, and then through a few of the roof tubes in the radiant heat section before being delivered to the atmospheric tower. The bottoms from the atmospheric

[12] *Petr. Zeit.*, **28** (21), 5.
[13] *Roads and Road Constr.*, 1933, **11**, 75; *J. Inst. Petr. Techn.*, 1933, **19**, 116A.
[14] *Nat. Petr. News*, 7.9.32, **24** (36), 26–35; *J. Inst. Petr. Techn.*, 1932, **18**, 468A.
[15] *Refiner*, 1932, **11**, 515; *J. Inst. Petr. Techn.*, 1933, **19**, 28A.

stage pass through the balance of the radiant section of the tube still and thence into the vacuum tower. Another plant is designed for processing cracking plant residuum. In this plant no tube still is required, as the hot residuum is received direct from the cracking unit and is pumped into the vacuum flash jug, while still hot. With the aid of highly superheated process steam the residue is stripped of all the lighter products, leaving a suitable asphalt.

McCabe[16] gives an interesting account of investigations on the possibility of using diphenyl vapour as a heating medium for heating asphalt. The experiments are described in Engineering Research Bulletin No. 23, July, 1932, issued by the Department of Engineering Research of the University of Michigan, Ann Arbor. A eutectic mixture of 20 per cent. diphenyl with 80 per cent. diphenyl oxide, which is liquid below room temperatures, is better than diphenyl, which has a melting point of 69° C. and may therefore give trouble by freezing in pipelines. In these investigations, full data were obtained on the heat transfer coefficients between diphenyl and asphalt, and also on the changes in properties of the asphalt during heating, which were very slight.

A method of obtaining improved quality of asphalt is claimed by Loebel,[17] who adds 20 per cent. of SO_2 extract (I.B.P. at least 250° C.) to an asphalt base oil and distils the mixture in the presence of air. He claims to obtain by this means an asphalt having a flatter penetration curve than that obtained by normal means from the same base oil.

The difficulty experienced in detaching asphalt completely from steel containers has given a lot of trouble in the past, and it is therefore of interest to note a method proposed by McConnell Sanders,[18] who applies a film consisting of a solution of an acid or an acid salt to the inside surface of the drum. He recommends the use of a solution of orthophosphoric acid combined with a chloride or nitrate of an alkali metal. The application of this solution causes the evolution of hydrogen at the surface of the metal, which serves as a cushion preventing the adherence of the asphalt to the metal.

Blowing.—One of the disadvantages of the old method of blowing asphalt is the enormous quantity of air required. According to Cross,[19] 300 cubic feet of air is required per barrel of oil at a temperature of 400° F. An improvement in the method of blowing has been introduced by the Turbo-Mixer Corporation,[20] who have

[16] *J. Inst. Petr. Techn.*, 1933, **19**, 29A.
[17] U.S.P. 1,881,753; *J. Inst. Petr. Techn.*, 1932, **18**, 469A.
[18] E.P. 381,632; *J. Inst. Petr. Techn.*, 1932, **18**, 469A.
[19] *Kansas City Testing Bulletin*, 25, 1931.
[20] *Refiner*, 1932, **11**, 521.

developed a device called the Turbo-oxidiser for inducing a powerful flow of air and to disperse this air in a very finely divided state, thereby presenting a much increased surface of air throughout the asphalt under treatment. They claim savings of 50 to 90 per cent. of the air formerly used.

The Standard Oil Co.[21] have designed a method for the continuous oxidation of hot petroleum residuum by the counter current application of air in a column, hot asphalt passing down and air upwards.

Treatment.—The turbo-mixer already referred to, can also be used for filling asphalt with slate dust. In one large refinery an eight-hour cycle was previously required to mix 20,000-gallon batches of asphalt and slate dust to a 50 per cent. slate dust content, which time cycle has been cut down to three hours. The same apparatus can also be used for the production of cut-backs and emulsions.

A method of rendering asphalt resistant to acids is claimed by Leckler.[22] The asphalt is melted or dissolved in an inert solvent, and then treated with one or more polymerising catalysts, which are enumerated. The asphalt is finally washed with alkali and water.

Application.

Road-Building.—A great deal of attention is being given to the behaviour of various types of mineral fillers used in road building. Searle[23] gives a comprehensive account of the use of fillers for asphalt, pitch and tar in road making. He draws attention to the importance of chemical inertness of the filler to the binder. For instance, acidic fillers like slate dust and brick dust are very inert, but basic fillers like limestone dust or Portland cement react with acidic components of pitch and tar, but are quite suitable for use with petroleum asphalt. An investigation by Evans[24] on the effect of mineral fillers on the physical properties of the mixture with asphalt, shows that the effect of the quantity and nature of the filler used, has so great an influence on the properties of the finished road that this effect easily masks small variations in the properties of the asphalt used. This subject is also dealt with by Taylor,[25] who gives a formula for the rise in melting point of the asphalt with increasing amount of fillers used. The formula is Rise$=K/\sqrt{D}$ where D is the average diameter

[21] E.P. 361,158; *J. Inst. Petr. Techn.*, 1932, **18**, 17A.
[22] E.P. 382,842; *J. Inst. Petr. Techn.*, 1933, **19**, 35A.
[23] *Roads and Road Constr.*, 1932, **10**, 332.
[24] *J. Inst. Petr. Techn.*, **18**, 957.
[25] *J.S.C.I.*, **53**, 415T; *J. Inst. Petr. Techn.*, 1933, **19**, 156A.

of the filler and K the stabilising power of the filler, varying with its type and the proportion present.

A new type of road surfacing[26] has been recently introduced in Europe consisting of the use of a mixture of Portland cement and asphalt. This binder is used for penetration macadam road surfacing, and is usually employed on well compacted water bound or bituminous macadam roads. This type of road surfacing has also recently been tried out in the U.S.A. on experimental stretches, with success.

The next International Road Congress will be held in Munich in 1934, and a preliminary programme has already been issued.[27] Amongst the subjects for discussion are the production and application of tar, asphalt and emulsion for roads, the methods of combating slipperiness of the road surface and the preparation and upkeep of cheap roads.

Rubber.—An important advance in rubber technique is the production of pulverised rubber from rubber latex.[28] To the powdered rubber, dextrin is added which prevents the rubber particles from sticking together so that the material can be transported in drums. This saves the transport on the 75 per cent. of water which is present in the latex. The powder is easily mixed with asphalt and road aggregates in an ordinary mixing drum by adding a small quantity of spirit. It is claimed that within an hour after pouring out the mixture a road can be released for traffic and that the cost of such a rubber road will probably be only slightly higher than the cost of a good asphalt road.

A good description of the use of asphalt in rubber technique is given by Adel.[29] It is pointed out that asphalt and pitch give true mixtures with rubber and have the effect of improving the plastic properties of the rubber. Tar and pitch mixtures, however, are susceptible to temperature changes whereas rubber mixtures with asphalt are not so susceptible.

Tar.—The world production of coal tar has declined[30] in recent years. The production in 1931, amounting to 6½ million metric tons, was 2 million tons less than in 1929, that is a decrease of about 23 per cent. The world demand for tar and tar products has not declined to anything like such an extent so that there is now a distinct shortage of tar and certain tar products, particularly pitch. The reduction in the production of tar was chiefly due to the reduced output of tar from coke-ovens in Germany and the U.S.A.

[26] *Engineering News Record*, 6.10.32, 400.
[27] *Petr. Zeit.*, **29** (13), 11.
[28] *Chem. Trade J.*, 1932, **91**, 165; *J. Inst. Petr. Techn.*, 1932, **18**, 387A.
[29] *Bitumen*, 1932, **2**, 50–54; *J. Inst. Petr. Techn.*, 1932, **18**, 173A.
[30] *Chem. Trade J.*, 9.12.32.

The consumption of road tar has not materially changed during the past two years, from 2 to 2½ million tons being used per annum calculated in terms of crude tar.

There is an extensive use of tar bitumen mixtures for road making and the extent to which tar can be blended with asphalt is dealt with by Temme[31] and by Pages and Houlnick.[32] Wieland[33] has a patent for producing a stable mixture of asphalt and tar. He adds lead oleate or resinate to the asphalt in sufficient quantity to give the asphalt the same surface tension and about the same specific gravity as the coal tar at the same viscosity. The asphalt is heated to bring it to the same viscosity as the coal tar before the mixing takes place. In this way a stable mixture of 70 per cent. of coal tar and 30 per cent. of asphalt is obtained. The mixture can be diluted with tar oil to the viscosity required for paving work.

The chemical structure of pitch has been investigated by Hugel and Frangopol[34] who examined the products obtained by hydrogenating pitch from Saare coal. They conclude that the pitch consists essentially of aromatic polycyclic hydrocarbons.

Miscellaneous Industrial Applications.—The use of asphalt for protecting concrete structures has been greatly extended. A description of the tests required for suitable grades for this work is given by Greger.[35] The principal applications are for protecting buttresses, pinion walls, brick or iron bridges and reservoirs. A priming coat is recommended of an asphalt solution in benzine, benzol or solvent naphtha as this has good penetrating power and forms a good surface for a second application of hot asphalt. If the bitumen coating is to remain durable, it should be protected as soon as possible after hardening by a suitable layer of stone material.

An interesting description of the method of preserving concrete piles with asphalt is given in a bulletin issued by the Union Oil Company of California.[36] The article describes the process of impregnating concrete blocks with asphalt in order to seal the surface against moisture and to prevent crystalline deposits in facial interstices of piling.

Great interest is being taken in the use of asphalt as insulating material in the electrical industries.[37] The addition of paraffin wax to the asphalt results in a blend which is flexible and free from

[31] *Bitumen*, 1932, **2**, 139, 143; *J. Inst. Petr. Techn.*, 1932, **18**, 434A.
[32] *Génie Civil*, **100**, 555.
[33] German Patent, 557, 375.
[34] *Ann. des Comb. Liq.*, 1932, **7**, 225–238, 417–467; *J. Inst. Petr. Techn.*, 1932, **18**, 467A.
[35] *Bitumen*, 1932, **2**, 151–156; *J. Inst. Petr. Techn.*, 1933, **19**, 38A.
[36] *Union Oil Co. of Calif. Bull.*, **13**, 7–11; *U.S. Bureau of Mines Abs.*, 1932, No. 4282.
[37] *Chem. Trade J.*, 1932, **91**, 318; *J. Inst. Petr. Techn.*, 1932, **18**, 434A.

cracks at low temperatures. Such a blend has very little stickiness and it has the important advantage of a low viscosity when melted, making it easy to fill the containers holding the electrical appliances. The important question of the formation of cracks in bituminous compounds for high-voltage ironclad switch gear has been studied by Dunton.[38] He describes an apparatus designed to study the effect of impact so that one can choose materials which do not develop hairline cracks under sudden vibration or shock. A suitable material in this respect is obtained by blending blown and steam distilled asphalts.

Emulsions.

Figures for the world production of asphalt emulsions are unobtainable, but the statistics issued by the U.S. Bureau of Mines[39] for the production in the U.S.A. give an indication of the importance of the asphalt emulsion industry in recent years. The production of petroleum asphalt and fluxes emulsified with water increased from 115,647 short tons in 1930 to 156,607 tons in 1931, an increase of more than 35 per cent. It is interesting to note that only about 10 per cent. of this production was made by the refineries actually manufacturing asphalt from crude petroleum. The remaining production was made by industrial companies which purchased the asphalt from the petroleum refineries.

It has occurred to many people that it might be more economical to transport a concentrated asphalt emulsion to the site of work, where the emulsion could be diluted to the concentration required for actual application to the road. It is shown, however, in an article in the Overseas Mechanical Transport Bulletin (Vol. IV., No. 3, p. 207), that emulsions containing more than 65 to 70 per cent. of asphalt are usually very viscous and if they are to be diluted without coagulation, the type of emulsifier used will make the final diluted emulsion too stable for ordinary road work. Where large quantities of asphalt emulsion are required, it is best to erect a local plant for the manufacture of the emulsion.

An interesting description is given by Wace[40] of the application of a special grade of asphalt emulsion for " mix-in-place " work as applied to the construction of landing grounds for aerodromes, playgrounds and footpaths. This method of using asphalt emulsion is also being tried out for roads carrying ordinary traffic, trial stretches having been laid down in England, Mexico, Germany, Sweden and Australia.

Among the useful applications of asphalt emulsion in roadwork,

[38] *J. Sci. Instr.*, 1932, **9**, 178; *J. Inst. Petr. Techn.*, 1932, **18**, 268A.
[39] *Oil & Gas J.*, 30.6.32, **31** (6), 27.
[40] *Overseas Mechanical Transport Bull.*, **4** (3), 201.

attention should be drawn to its use for curing concrete roads when applied within a few hours of the pouring of the concrete.[41]

Much attention continues to be given to the chemical and physical problems associated with the preparation and application of asphalt emulsions. In an interesting paper read by Clayton to the Chemical Engineering Group of the Society of Chemical Industry on November 25th, 1932, on "Problems of Emulsion Persistence," the author referred to the work which has been carried out on asphalt emulsions for road application, pointing out that at present our views on this subject are of an empirical nature. He drew attention to a number of problems which still await accurate quantitative elucidation before an adequate scientific control could be exercised over the application of asphalt emulsions to road work.

Among some of the more important investigations on the chemistry and physics of asphalt emulsions, attention should be drawn to a series of investigations carried out by Traxler and Pittman[42] on the interfacial tension between asphaltic materials and various aqueous solutions, and the study of the stabilisation of aqueous dispersions of asphalt by Hixon and Fain.[43] Vellinger and Flaigny[44] show that the stability of asphalt emulsions is related to the pH value of the aqueous phase. Weber and Bechler[45] have studied the break-down of asphalt emulsion with various types of stone. They have devised a method of measuring the "breakdown value" (Zeifallswert), and have come to the conclusion that one cannot generalise from the behaviour of an emulsion with a given stone. The actual aggregate which is to be used must be investigated as to its breakdown value in every instance.

Specifications and Testing.

The chaotic condition of the testing of liquid asphaltic products is illustrated by the fact that in the U.S.A. there are several hundred specifications for these products. A rational scheme for a standardisation of the tests used was put forward last year so as to eliminate unnecessary tests and to introduce uniformity in the tests which are retained. Recommendations on the rationalisation and simplification of test requirements for liquid asphaltic materials are given by Kelley, of the U.S. Bureau of Public Roads, and

---

[41] *Roads & Road Constr.*, 1932, **10**, 242.

[42] *Ind. Eng. Chem.*, 1932, **24**, 1003–1005, 1391; *J. Inst. Petr. Techn.*, 1932, **18**, 386A.

[43] *Ind. Eng. Chem.*, 1932, **24**, 1336; *J. Inst. Petr. Techn.*, 1933, **19**, 24A.

[44] *Ann. des Comb. Liq.*, 1932, **7**, 217–224; *J. Inst. Petr. Techn.*, 1932, **18**, 433A.

[45] *Asphalt u. Teer*, 1932, **32**, 45–49, etc.; *J. Inst. Petr. Techn.*, 1932, **18**, 265A.

Hubbard, of the Asphalt Institute.[46] They recommend the following four tests: Flashpoint, Viscosity, Distillation and examination of the Residue from the Distillation Test. The Asphalt Institute of the U.S.A. have issued a set of thirteen specifications, which replace the seven tentative specifications issued by that body last year. The thirteen specifications classify liquid asphaltic road materials into three groups: R.C., or rapid curing cut-back asphalts; M.C., or medium curing cut-back asphalts; and S.C., or slow curing products. A table is given of the principal uses of the materials meeting the specifications recommended by the Asphalt Institute. These specifications are based on the tests recommended by Kelley and Hubbard mentioned above.

A review of the present position regarding the testing of asphalt and asphalt paving mixtures is given in the two papers, already mentioned, by Taylor[25] and by Baskin[3]; the latter draws attention to the very limited value of the usual tests which are stipulated in present-day specifications.

The recovery of asphalt from solutions without altering its properties is an important step in the examination of samples taken from finished roads. Greutert[47] describes a method which is a modification of that used by Suida, and in which carbon bisulphide is used as the solvent and the distillation is carried out under reduced pressure in an atmosphere of carbon dioxide. This method has been found to be successful, showing very small hardening of the asphalt during the recovery from solution.

Nellensteyn and Kuipers[48] describe a method of estimating asphalt in mixtures with tar, which is claimed to be reliable for mixtures containing up to 50 per cent. of asphalt, but is less accurate when the asphalt content is higher.

A penetrometer suitable for testing samples of mastic asphalt is described by Wolf.[49] The instrument is similar in principle to the standard asphalt penetrometer, but the needle of the latter is replaced by a stout rod, higher loads and longer contact periods being used. The use of the instrument is limited to mastics, which are free from mineral particles having an average diameter greater than one-tenth of the plunger. For samples containing coarse sand, grit or chippings, a plunger of larger cross section would be required and consequently much heavier weights to give the same load per unit area. A suitable instrument for this purpose is to be constructed.

---

[46] *Public Roads*, August, 1932, **13**, 89.
[47] *J. Inst. Petr. Techn.*, 1932, **18**, 846.
[48] *Bitumen*, 1932, **2**, 133–134; *J. Inst. Petr. Techn.*, 1932, **18**, 408A.
[49] *J. Sci. Instr.*, 1932, **9**, 22; *J. Inst. Petr. Techn.*, 1932. **18**. 91A.

The important property of the adhesion of asphalt to mineral aggregate continues to receive attention. Nicholson[50] discusses mathematically the principles underlying the adhesion of asphalt to aggregate in the presence of water and puts forward two laboratory tests for measuring the adhesion. In one test the coated aggregate is covered with water at 140° F., and shaken for one hour, after which the quantity of uncovered aggregate is measured. In the other test, the coated aggregate is covered with varying quantities of benzole, and after standing for two hours water is added and the whole shaken for one hour. The amount of uncovered aggregate is then measured. The amount of benzole required which will remove the asphalt from the stone is a measure of the adhesion. Fricke and Meyring[51] estimate the adhesive or wetting power of road tars and mixtures of asphalt and tar, from the measurement of the marginal angle of contact of drops upon glass surfaces.

---

[50] *Roads & Streets*, 1932, **75**, 237.
[51] *Asphalt u. Strassenbau*, 1932, **32**, 264–273.

Special Products.

By E. B. Evans, M.Sc., A.I.C. (Assoc. Member).

The production and utilisation of "special products" and synthetic chemicals from petroleum continues to expand rapidly. Much useful work has been accomplished during the year 1932 on the better known products such as waxes and transformer oils, but very much more remains to be done with regard to utilising the immense supplies of natural and refinery gases. In many cases natural gas still has to be burned to waste, solely because no profitable outlet has been found for the production in the remoter fields.

Nevertheless, the development of the synthetic chemical industry has been rapid, and the recent appearance in commercial quantity of many materials useful in the industry has been due to progress in this field.

The work published on the various products covered will be reviewed briefly in the following sections.

Naphthenic Acids.

Pilat and Reyman[1] have investigated the nature of the naphthenic acids prepared from Galician crude oil and from its distillates. Similar acids are present, but the authors consider the mixture of acids in the crude to be far more complex than that in the distillate. The formation of naphthenic acids is discussed by Petrov and Ivanoff,[2] who conclude, from a comparison of acids obtained by oxidation of gas oil and by cracking of oleic acid, that the products occurring in petroleum are formed partly by cracking and cyclisation of the fatty acids present in the mother substance of petroleum, and partly by oxidation of naphthenes and polynaphthenes in air. Luft[3] has investigated Charitschkoff's reaction with regard to its sensitivity and specificity. It is considered by Schmitz[4] that naphthenic acids are best prepared by the neutralisation of crude oils or distillates before further treatment. The whole problem of the neutralisation of crude oils is discussed, together with the "salt process" of extraction. A paper by von Braun[5] summarises some modern views on the nature of naphthenic acids in petroleum.

The use of metal naphthenates in paints and varnishes is dealt with in an anonymous article.[6] The incorporation of naphthenates

[1] *Ann.*, 1932, **499**, 76; *J. Inst. Petr. Techn.*, 1932, **18**, 478A.
[2] *J.A.C.S.*, 1932, **54**, 239; *J. Inst. Petr. Techn.*, 1932, **18**, 104A.
[3] *Petr. Z.*, 15.6.32, **28** (24), 16; *J. Inst. Petr. Techn.*, 1932, **18**, 360A.
[4] *Erdöl u. Teer*, 1932, **8**, 27, 44; *J. Inst. Petr. Techn.*, 1932, **18**, 128A.
[5] *Z. angew. chem.*, 1931, **44**, 661; *Nat. Petr. News*, 24.2.32, **24** (8), 28; *J. Inst. Petr. Techn.*, 1932, **18**, 184A.
[6] *Chem. Trade J.*, 1932, **91**, 238; *J. Inst. Petr. Techn.*, 1932, **18**, 437A.

reduces the oil absorption of pigments. Aluminium naphthenates (in particular) hinder the settling out of pigments from oils or varnishes.

Butane and Similar Products.

The use of butane gas in the U.S.A. for heating purposes has expanded rapidly in the last few years. The gas is distributed in liquefied form and is largely used for refrigerating plants, orchard heating, welding and many other purposes.[7] Details of the plant for preparing propane and butane has also been given.[8]

The dew-points of hydrocarbons are very important properties in connection with the distribution and use of liquefied gas. Hachmuth[9] gives data for a number of gases and finds Raoult's Law to apply accurately to mixtures of paraffin hydrocarbons.

The economics of the liquefied gas production are discussed by Kremser.[10]

Acid Sludge.

The utilisation and disposal of acid sludge still presents problems. A burner which is claimed to be satisfactory for handling acid sludge direct from the process is described by Anderson.[11] The atomisation is by means of steam, and the air is given a rotary motion before impinging on the atomised fuel.

A description of Hamburger's method for recovery of acid sludge, which is said to yield also a bitumen suitable for use in roofing-felts, acid-resisting paints, etc., is given in an anonymous paper.[12] A du Pont patent describes the recovery of sulphuric acid as ammonium bisulphate by treatment with an aqueous sulphuric acid solution of ammonium sulphate.[13]

Petroleum Coke.

The use of petroleum coke as a refinery fuel is steadily increasing, and suitable equipment for handling it is being produced. The progress is described by Staley[14] and by Campbell.[15] The nature and properties of petroleum coke are dealt with by Morrell and Egloff.[16]

---

[7] *Oil & Gas J.*, 7.4.32, **30** (47), 22; *J. Inst. Petr. Techn.*, 1932, **18**, 208A.
[8] *Refiner*, 1932, **11**, 215.
[9] *Ind. Eng. Chem.*, 1932, **24**, 82; *J. Inst. Petr. Techn.*, 1932, **18**, 82A.
[10] *Refiner*, 1932, **11**, 360; *J. Inst. Petr. Techn.*, 1932, **18**, 298A.
[11] *Refiner*, 1932, **11**, 241; *J. Inst. Petr. Techn.*, 1932, **18**, 177A.
[12] *Rev. Petr.*, 9.4.32, (470), 437; *J. Inst. Petr. Techn.*, 1932, **18**, 220A.
[13] E.P. 365,945, 28.1.32; *J. Inst. Petr. Techn.*, 1932, **18**, 130A.
[14] *Petr. Eng.*, Feb., 1932, **3** (5), 20; *J. Inst. Petr. Techn.*, 1932, **18**, 174A.
[15] *Refiner*, 1932, **11**, 576.
[16] *J.S.C.I.*, 1932, **51**, 467; *J. Inst. Petr. Techn.*, 1932, **18**, 267A.

Carbon Black.

Carbon black is produced by cracking natural gas by the "Thermatomic" process.[17] The product is stated to be very suitable for incorporation in rubber compounds. A description of a carbon black plant at Taihei, Japan, is given by Matsusawa.[18] Excellent yields are claimed. The moisture sorptions for a number of carbon blacks are presented by Dewey and Lefforge.[19] The method of examination is given, and it is concluded that the figures obtained experimentally were in good agreement with the deduction from the results of determinations of volatile contents. The effects of grit in carbon blacks on the properties of vulcanised rubber is discussed by Street.[20]

Hydrocarbon Solvents.

An important development in this field is the production of a range of hydrogenated solvents, which have excellent solvent powers for gums and resins—equal in fact to the coal-tar aromatic hydrocarbons. It is anticipated that a number of these will shortly be available commercially for use in the paint, lacquer and rubber industries.[21] The use of hydrocarbon solvents in paints and varnishes is discussed by Blin.[22]

A valuable survey of the solvents derived from the gas industry is given by Downs.[23] Brown[24] states that the best soap for use with benzene in dry-cleaning consists of potash-soap containing 5 per cent. to 10 per cent. of free fatty acid; about one part of this should be used in 400 of benzene. Dry-cleaning spirit may be recovered by treatment with chloride of lime and alkali according to a patent by Miller.[25]

Insecticides.

Although unsaturated hydrocarbons have a high toxic power towards insects, Gothard[26] considers that the odour of cracked distillates renders them unsuitable for household use in insecticides,

---

[17] Moore, *Ind. Eng. Chem.*, 1932, **24**, 21; *Chem. Met. Eng.*, 1932, **39**, 380; *J. Inst. Petr. Techn.*, 1932, **18**, 82A.

[18] *Oil & Gas J.*, 17.5.32, **30** (51), 76. *J. Inst. Petr. Techn.*, 1932, **18**, 267A.

[19] *Ind. Eng. Chem.*, 1932, **24**, 1045; *J. Inst. Petr. Techn.*, 1932, **18**, 388A.

[20] *Ind. Eng. Chem.*, 1932, **24**, 559.

[21] *Ind. Eng. Chem.*, 1932, **24**, 1129; *J. Inst. Petr. Techn.*, 1932, **18**, 444A.

[22] *Mat. Grasses*, 1932, (288), 9472; *J. Inst. Petr. Techn.*, 1932, **18**, 312A.

[23] *J.S.C.I.*, 1932, **51**, 28, 45; *J. Inst. Petr. Techn.*, 1932, **18**, 75A.

[24] *Chem. Trade J.*, 22.7.32, **91**, Suppl. IV.; *J. Inst. Petr. Techn.*, 1932, **18**, 351A.

[25] U.S.P. 1,878,287, 20.9.32; *J. Inst. Petr. Techn.*, 1932, **18**, 437A.

[26] *Manuf. Chem.*, 1932, **3**, 170; *J. Inst. Petr. Techn.*, 1932, **18**, 311A.

and consequently straight-run distillates must be employed. Information is given on the specifications of benzines employed. Another paper dealing with this subject is that of Richardson,[27] who found that the higher boiling fractions of Midcontinent oils had a greater insecticidal value than the lower ones. The effect of the kerosene used in preparing household sprays is at least as important as that of the pyrethrum. Distillates of boiling-range of about 190–270° C. are very suitable; heavier distillates tend to leave residues about the house.

For use in spraying, only emulsifiers which give stable oil-in-water emulsions can be used.[28] Water-in-oil emulsions are suitable for weed-killers. Formulæ for the preparation of insecticides are given by Woodman and also by Caplan.[29] Numerous patents have been taken out for insecticides.[30].

Paraffin Wax.

Katz[31] has continued his work on the crystallisation of paraffin wax. He has shown that the needle form of crystal can only be produced from solutions where the concentration of wax is greater than the "concentration of change" for the given wax and solvent. The "temperature of change" is the saturation temperature corresponding to the concentration of change and is some 5 to 10° C. below the melting point of the wax present in the solution. Below the concentration of change plate crystals are deposited. Ivanovszky[32] considers that ozokerite and paraffin can best be characterised by their behaviour in the form of pastes with benzene. He introduces the conception of "retention number" of a wax and shows how it varies for mixtures of paraffin and ozokerite.

The separation of normal paraffin hydrocarbons from C_{20} to C_{30} by distillation in high vacuum has been studied by Gilchrist and Karlik.[33] Investigations on the solubility of oils and waxes in organic solvents have been continued by Poole and Mangelsdorf,[34] who have developed general equations giving the quantity of wax dissolved by oil-solvent mixtures. The appropriate constants for

[27] *Ind. Eng. Chem.*, 1932, **24**, 1394; *J. Inst. Petr. Techn.*, 1933, **19**, 39A.
[28] *J.S.C.I.*, 1932, **51**, 358T; *J. Inst. Petr. Techn.*, 1932, **18**, 469A.
[29] *Petr. Eng.*, Dec., 1932, **4** (3), 50; *J. Inst. Petr. Techn.*, 1933, **19**, 112A.
[30] I. G. Farbenind. A.-G., E.P. 377,069, 21.7.32; 378,300, 11.8.32; Piotrowski and Winkler, U.S.P. 1,869,231, 26.7.32; *J. Inst. Petr. Techn.*, 1932, **18**, 352A, 389A, 390A.
[31] *J. Inst. Petr. Techn.*, 1932, **18**, 37.
[32] *Erdöl u. Teer*, 1932, **8**, 477; *J. Inst. Petr. Techn.*, 1932, **18**, 465A.
[33] *J.C.S.*, 1932, **135**, 1992; *J. Inst. Petr. Techn.*, 1932, **18**, 404A.
[34] *Ind. Eng. Chem.*, 1932, **24**, 1215; *J. Inst. Petr. Techn.*, 1933, **19**, 16A.

about forty solvents have been calculated. Fussteig[35] describes an apparatus for sweating paraffin wax and claims great economy and efficiency. The properties of ozokerite are discussed in an anonymous article.[36] It is stated that the material is particularly suitable for electrical purposes on account of its freedom from brittleness. Another article[37] deals with the use of paraffin wax in the preparation of leather-currying greases.

Synthetic Chemicals from Petroleum.

Much attention continues to be given to the development of a chemical industry based on petroleum as a raw material, and the operations involved in the utilisation of light hydrocarbons and cracking-still gases are coming to be regarded as normal refinery processes. A symposium[38] on the utilisation of gaseous hydrocarbons includes a number of useful papers. The use of these gases as raw materials is discussed by Frolich and Wiezevich[39] and Bowen.[40] A valuable paper on the physico-chemical properties of methane is that of Storch.[41] Markovitch and Pigulevsky[42] have examined the composition and properties of the gas from vapour-phase cracking and consider that it is the most promising source of material for chemical industry.

The production of the amyl alcohols and amyl acetates by the chlorination of pentanes is described by Bohall.[43] A number of patents deal with the absorption of olefines in sulphuric acid for the production of ethyl and other alcohols.[44] The conversion of cracking-still gases into alcohols is described in a refining article.[45] The production of glycols from chlorohydrins is covered by Dunstan and Birch.[46]

The requirements of good refrigerants are stated by Waterfill,[47]

---

[35] *Mat. Grasses*, 1932, (288), 9480; *J. Inst. Petr. Techn.*, 1932, **18**, 307A.
[36] *Chem. Trade J.*, 1932, **91**, 75; *J. Inst. Petr. Techn.*, 1932, **18**, 89A.
[37] *Chem. Trade J.*, 1932, **91**, 142; *J. Inst. Petr. Techn.*, 1932, **18**, 93A.
[38] *Ind. Eng. Chem.*, 1932, **24**, 10; *J. Inst. Petr. Techn.*, 1932, **18**, 81A.
[39] *Ind. Eng. Chem.*, 1932, **24**, 13; *J. Inst. Petr. Techn.*, 1932, **18**, 81A.
[40] *Oil & Gas J.*, 31.3.32, **30** (46), 88; *J. Inst. Petr. Techn.*, 1932, **18**, 226A.
[41] *U.S. Bur. Min. Inf. Circ.* 6549; *J. Inst. Petr. Techn.*, 1932, **18**, 119A.
[42] *Refiner*, 1932, **11**, 256, 303, 348; *J. Inst. Petr. Techn.*, 1932, **18**, 159A, 222A, 275A.
[43] *Refiner*, 1932, **11**, 438; *J. Inst. Petr. Techn.*, 1932, **18**, 387A.
[44] Horsley and I.C.I. Ltd., E.P. 369,216 (15.3.32); Distillers Co. and others, E.P. 368,051 (3.3.32), 370,136 (7.4.32); N. V. Bataafsche Petr. Mij., E.P. 360,331 (5.11.31), 378,764 (18.8.32); Brit. Indust. Solvents, E.P. 381,185 (26.9.32); *J. Inst. Petr. Techn.*, 1932, **18**, 218A, 175A, 219A, 59A, 470A.
[45] *Refiner*, 1932, **11**, 224.
[46] E.P. 365,589, 18.1.32; *J. Inst. Petr. Techn.*, 1932, **18**, 130A.
[47] *Ind. Eng. Chem.*, 1932, **24**, 616; *J. Inst. Petr. Techn.*, 1932, **18**, 268A.

who considers that dichloro-methane and dichloroethylene are excellent materials for this purpose. Carlisle and Levine[48] examined the stabilities of some chlorinated hydrocarbons. Methylene chloride is stable up to about 120° C.; trichloroethylene is a very stable compound.

The catalytic oxidation of hydrocarbon vapours is discussed very fully in a recently published book by Marek and Hahn,[49] which includes the oxidation of gaseous paraffins and petroleum oils and the oxidation and hydration of unsaturated hydrocarbons.

The mechanism of the oxidation of petroleum hydrocarbons to oxygen compounds such as aldehydes and ketones, acids, ethers and alcohols is also discussed in a series of papers by Beall,[50] who reviews the available literature on the subject. Marek[51] describes the oxidation of hydrocarbons and the apparatus employed. Schultz and White[52] have examined the mechanism and reaction velocity of the oxidation of Pennsylvanian naphtha in comparison with the cracking reaction. The oxidation of light petroleum hydrocarbons is discussed by Pidgeon and Egerton,[53] and the oxidation of p-cymene by Senseman and Stubbs.[54] Bibb[55] finds that oxides of nitrogen catalyse the oxidation of natural gas. The properties of aliphatic ketones as solvents are discussed by Park and Hofmann.[56] Hofmann[57] has contributed an interesting study of the evaporation rates of organic liquids.

Synthetic resins may be obtained from petroleum by the polymerisation of olefines and diolefines.[58] Nugey[59] considers the production of ethylene from cracking-still gases as raw material for the preparation of these resins, while their use as protective coatings is included in a paper by Deacon.[60]

---

[48] *Ind. Eng. Chem.*, 1932, **24**, 146, 1164; *J. Inst. Petr. Techn.*, 1932, **18**, 436A.

[49] "Catalytic Oxidation of Organic Compounds in the Vapour Phase," A.C.S. Monograph 61, Chemical Catalog Co., 1932.

[50] *Refiner*, 1932, **11**, 390, 422, 463, 606; *J. Inst. Petr. Techn.*, 1932, **18**, 299A, 388A.

[51] *Ind. Eng. Chem.*, 1932, **24**, 1103.

[52] *Ind. Eng. Chem.*, 1932, **24**, 1277; *J. Inst. Petr. Techn.*, 1932, **18**, 475A.

[53] *J.C.S.*, 1932, **135**, 661, 676; *J. Inst. Petr. Techn.*, 1932, **18**, 138A.

[54] *Ind. Eng. Chem.*, 1932, **24**, 1184.

[55] *Ind. Eng. Chem.*, 1932, **24**, 10; *J. Inst. Petr. Techn.*, 1932, **18**, 81A.

[56] *Ind. Eng. Chem.*, 1932, **24**, 132.

[57] *Ind. Eng. Chem.*, 1932, **24**, 135.

[58] *Ind. Eng. Chem.*, 1932, **24**, 1125; *J. Inst. Petr. Techn.*, 1932, **18**, 448A.

[59] *Refiner*, 1932, **11**, 547.

[60] *Oil & Gas J.*, 1.9.32, **31** (15), 33; *J. Inst. Petr. Techn.*, 1932, **18**, 435A.

Transformer Oils.

Very little work seems to have been published on transformer oils during the past year, except in regard to methods of testing.[61] Müller and Consolati[62] have examined the effect of artificial ageing of new and used oils by the Weiss and Salomon method. Oxidation of insulating oils causes a marked increase in spreading power and in high-frequency dielectric losses.[63] A series of experiments with insulating oils was carried out by Typke,[64] using an experimental type of transformer. The result of the ordinary laboratory test-methods did not generally agree with the results of the transformer tests. It is suggested that the minimum requirement of an oil as regards stability should be that it passes the B.S.I. Class B specification—not over 0·8 per cent. sludge. Creangă[65] is of the opinion that Rumanian crude oils are generally unsuitable for the production of transformer oils, although in certain cases good products may be obtained by careful refining. The Edeleanu process is very suitable for refining transformer oils.[66]

Miscellaneous.

The preparation of specialities such as polishes, cosmetics and cutting oils are described by Staley[67] and Caplan.[68]

The American Government plant at Amarillo, Texas, is producing large quantities of helium from a natural gas containing about 2 per cent. of the element.[69] Another element obtained as a by-product is iodine, which is prepared from the well-waters of Surabaya, Java,[70] in which occur appreciable quantities of magnesium iodide. Ammonia is produced in a Californian plant from hydrogen prepared from natural gas, this being combined with atmospheric nitrogen by the Mont Cenis process.[71]

The Girdler process for the manufacture of carbon dioxide is

---

[61] Italian Electro-Technical Assoc., *Olii. Min.*, 1932, **12**, 50, 65; *J. Inst. Petr. Techn.*, 1932, **18**, 308A.

[62] *Erdöl u. Teer*, 1932, **8**, 525, 540, 557; *J. Inst. Petr. Techn.*, 1933, **19**, 54A.

[63] Race, *J. Phys. Chem.*, 1932, **36**, 1928; *J. Inst. Petr. Techn.*, 1932, **18**, 343A.

[64] *Erdöl u. Teer*, 1932, **8**, 170, 186; *J. Inst. Petr. Techn.*, 1932, **18**, 214A.

[65] *Petr. Z.*, 8.6.32, **28** (23), 1; *J. Inst. Petr. Techn.*, 1932, **18**, 377A.

[66] Kain, *Refiner*, 1932, **11**, 553; *J. Inst. Petr. Techn.*, 1933, **19**, 27A.

[67] *Petr. Eng.*, July, 1932, **3** (11), 31; *J. Inst. Petr. Techn.*, 1932, **18**, 351A.

[68] *Petr. Eng.*, May, 1932, **3** (8), 47; *J. Inst. Petr. Techn.*, 1932, **18**, 311A.

[69] *Petr. Eng.*, Sept., 1932, **3** (13), 102; *J. Inst. Petr. Techn.*, 1932, **18**, 429A.

[70] *Chem. Trade J.*, 1932, **90**, 451; *J. Inst. Petr. Techn.*, 1932, **18**, 267A.

[71] Rosenstein, *Chem. Met. Eng.*, 1931, **38**, 636; *J. Inst. Petr. Techn.*, 1932, **18**, 57A.

described in several papers.[72] "Dry ice" is prepared from the gas by the Frick process.[73] The purification and drying of the gas before solidification may be carried out by Silica Gel treatment.[74]

It has been proposed to use spent refinery clay in the manufacture of a water-proof Portland cement. About 3 per cent. of clay is used, and the product is said to be stronger than the straight cement.[75]

Antirust compositions containing mineral jellies are in general use for protecting metals.[76] The use for this purpose of bitumen dispersed in aqueous lignic or humic acids has also been patented.[77]

---

[72] *Refiner*, 1932, **11**, 218; Albright, *Refiner*, 1932, **11**, 19; *J. Inst. Petr. Techn.*, 1932, **18**, 83A; Campbell, *Oil & Gas J.*, 19.5.32, **30** (53), 41; *J. Inst. Petr. Techn.*, 1932, **18**, 268A.

[73] *Refiner*, 1932, **11**, 220.

[74] *Refiner*, 1932, **11**, 222.

[75] *Nat. Petr. News*, 27.7.32, **24** (30), 31; *J. Inst. Petr. Techn.*, 1932, **18**, 394A.

[76] Marsh and Mills, *Aircraft Eng.*, 1932, **4**, 57; *J. Inst. Petr. Techn.*, 1932, **18**, 144A.

[77] Groves, E.P. 369,242, 8.3.32; *J. Inst. Petr. Techn.*, 1932, **18**, 218A.

Analysis and Testing.

By W. H. Thomas, A.R.S.M. (Member).

During the year 1932, a certain amount of concerted effort has been made towards the elucidation of some of the more pressing problems of petroleum analysis. This, it will be seen, is particularly the case with regard to work on viscosity determination and the development of laboratory distillation. Another interesting feature is the increasing amount of attention which is being paid to the systematic determination of physical constants, a subject which until comparatively recently had been largely ignored. This deficiency has been to some extent overcome by the publication of "Technical Data on Fuel," edited by Spiers, a third edition of which has been issued.

The analysis and examination of lubricants has also commanded a good deal of attention, but in this section certain problems, such as the development of a really satisfactory oxidation test, have been practically neglected or only subjected to sporadic work of a rather nebulous character.

Among the publications of 1932, the A.S.T.M. has issued the report of Committee D. 2 on Petroleum Products and Lubricants, giving the latest form of revisions accepted at the June meeting of this committee. Mention should also be made of the second edition of "Analysis of Petroleum Products in and for U. S. S. R." by Dobriansky. Most of the methods described are those universally used, but some have been developed to meet local conditions.

With regard to standard apparatus, no new types or modifications have appeared on the market during 1932, but it is evident that electric heating and automatic temperature control are being more extensively applied.

In the following remarks, it is proposed to follow the procedure adopted in previous reports on this subject and to divide the more detailed matter under suitable headings.

Crude Oil.

Other than the assay of crude oils by laboratory distillation, there is little to comment upon with regard to the analysis of crude oils. Luft,[1] however, has discussed Charitschkoff's reaction with respect to its limits of sensitivity in the detection of napthenic acids. The reaction depends on the formation of green, benzene-soluble, copper naphthenates on the addition of copper sulphate solution to the fractions containing naphthenic acids. For the estimation of paraffin wax in crude petroleum, a variation of the

[1] Luft, *Petr. Z.*, 1932, **28** (24), 16; *J. Inst. Petr. Techn.*, 1932, **18**, 360A.

Eugler-Holde method has been described,[2] in which the chief modification lies in the preparation of the sample by two stages of distillation. The characteristic fluorescences of various petroleum oils and waxes under ultra-violet light have been shown[3] to be a valuable adjunct to analysis and the detection of adulterants. A very significant contribution is that of Maillard, Vellinger and Verdier,[4] on the solubility of oxygen in mineral oils. These authors have shown that although the nature and origin of the oil do not appear to have any marked effects, there is an inversion of the case of oxidation as a function of refining, as one passes from normal to high temperatures.

Gas.

The analysis of hydrocarbon gases has continued to afford a fruitful if somewhat limited field of work, the methods dealt with being both chemical and physical. One method proposed[5] is to divide the gas into a condensate and a permanent gas. The former is fractionated and examined, while the latter is analysed in the normal way. MacGillivray[6] has described the preparation of pure ethane, methane and hydrogen, together with methods for analysis of their mixtures. Details of an improved form of gas absorption pipette have been published,[7] while by extending the Bureau of Mines method of fuel gas analysis to include an additional combustion with oxygen, Watson and Ceaglske[8] have obtained results which may be used for combustion calculations. A physical method of analysis has been developed by van Dyck,[9] based on the difference in solubility of gases in a liquid. In the determination of olefines by hydrogenation[10] it was found that one volume of hydrogen disappeared for each double bond and hence, the contraction showed the olefine content directly. The use of the wet and dry bulb method for estimating the relative humidity of gas has been suggested[11] in view of the fact that injection of oil and moisture into pipe lines carrying dry natural gas is necessary

[2] Chmélevsky, *Rev. Petr.*, 6.8.32, (487), 982; *J. Inst. Petr. Techn.*, 1932, **18**, 361A.
[3] Muir, *Ind. Chem.*, 1932, **8**, 324; *J. Inst. Petr. Techn.*, 1932, **18**, 480A.
[4] Maillard, Vellinger and Verdier, *Ann. des Comb. Liq.*, 1932, **7**, 7; *J. Inst. Petr. Techn.*, 1932, **18**, 364A.
[5] Davis and Daugherty, *Ind. Eng. Chem. Anal.*, 1932, **4**, 193; *J. Inst. Petr. Techn.*, 1932, **18**, 230A.
[6] MacGillivray, *J.C.S.*, 1932, **135**, 941; *J. Inst. Petr. Techn.*, 1932, **18**, 188A.
[7] Tramm, *Brenn.-Chem.*, 1932, **13**, 146; *J. Inst. Petr. Techn.*, 1932, **18**, 230A.
[8] Watson and Ceaglske, *Ind. Eng. Chem. Anal.*, 1932, **4**, 70; *J. Inst. Petr. Techn.*, 1932, **18**, 106A.
[9] Van Dyck, *J. Inst. Petr. Techn.*, 1932, **18**, 145.
[10] Skärblom, *Brenn.-Chem.*, 1932, **13**, 452.
[11] Frymoyer, *Oil & Gas J.*, 1.9.32, **31** (15), 12; *J. Inst. Petr. Techn.*, 1932, **18**, 451A.

to prevent leakage from joints, meters, etc. An apparatus embodying Haldane's principle has been evolved[12] for the determination of combustible vapours in the atmosphere, and Pachtner[13] has determined the explosion limits of oil vapour-air mixtures. A redesigned form of Renarex carbon dioxide indicator has been described,[14] and in a somewhat similar connection Fox and Groves[15] have given a description of an automatic recorder for sulphur acids in flue gases.

With regard to gas flow, Killeffer[16] has used the thermal characteristics of the gas as a means of measurement by noting the change of temperature of the gas when supplied with a measured heat input. A resistance-tube type of flowmeter for small rates of gas flow has been described,[17] and Yuster[18] is responsible for a method of obtaining a wide range in rates of gaseous flow, in which glass capillaries are used in series with the gas flow. An apparatus for the continuous determination of quantities of gas absorbed in a liquid[19] and one for indicating the specific gravity of gases[20] have been patented. Finally, it is of interest to note that Storch[21] has given a condensed review of the physical and chemical properties of methane.

Motor Fuel.

Apart from the estimation of anti-knock value of motor fuels, the tests which at present are of next importance and which have been subjected to the greatest amount of investigation are those concerning existent and potential gum content.

The estimation of the existent gum content of cracked motor fuels has continued to receive attention,[22] and attempts are being made to standardise a test which in all probability will comprise an air-jet method.[23] The A.S.T.M. have published two suggested

[12] McNair and Gull, *Analyst*, 1932, **57**, 159; *J. Inst. Petr. Techn.*, 1932, **18**, 187A.
[13] Pachtner, *Petr. Z.*, 2.7.32, **28** (4), 1; *J. Inst. Petr. Techn.*, 1932, **18**, 108A.
[14] *Instr. Wld.*, 1932, **4**, 231; *J. Inst. Petr. Techn.*, 1932, **18**, 189A.
[15] Fox and Groves, *J.S.C.I.*, 1932, **51**, 7T; *J. Inst. Petr. Techn.*, 1932, **18**, 97A.
[16] Killeffer, *Ind. Eng. Chem. Anal.*, 1932, **4**, 97; *J. Inst. Petr. Techn.*, 1932, **18**, 106A.
[17] Smith, *Ind. Eng. Chem. Anal.*, 1932, **4**, 244; *J. Inst. Petr. Techn.*, 1932, **18**, 232A.
[18] Yuster, *Ind. Eng. Chem. Anal.*, 1932, **4**, 224; *J. Inst. Petr. Techn.*, 1932, **18**, 233A.
[19] E.P. 363,369; *J. Inst. Petr. Techn.*, 1932, **18**, 97A.
[20] E.P. 381,170; *J. Inst. Petr. Techn.*, 1932, **18**, 474A.
[21] Storch, *U.S. Bur. Mines Inf. Circ.* 6549; *J. Inst. Petr. Techn.*, 1932, **18**, 119A.
[22] Yale and Wilson, *Ind. Eng. Chem.*, 1931, **23**, 1254; *J. Inst. Petr. Techn.*, 1932, **18**, 31A.
[23] Mulligan, Lovell and Boyd, *Ind. Eng. Chem. Anal.*, 1932, **4**, 351; *J. Inst. Petr. Techn.*, 1932, **18**, 479A.

methods,[24] while the I.P.T. has an air-jet method under consideration. Ramsay[25] has studied the variables of the oxygen-bomb method for the estimation of induction period, and suggests that if the determination be made at two or three temperatures, then the period of stability of a sample at atmospheric temperature and pressure may be predicted with a fair degree of accuracy. Aldrich and Robie,[26] working on the same problem, have arrived at similar conclusions. They consider, however, that the procedure does not permit determinations of induction period at sufficiently low temperatures to render extrapolation to storage temperatures reasonably accurate. Bridgeman,[27] studying gum formation, has investigated the effect of bath temperature on results and has compared them with those of the steam-oven and air jet methods. This author doubts whether the induction period gives a real indication of gum stability. Under the auspices of the U.S. Naval Department, an accelerated oxidation test for motor fuels has been adopted,[28] the apparatus used being a modification of that of Hunn, Fischer and Blackwood. Klöttner's and Jacqué's methods for the determination of potential gum have been discussed,[29] the former's method being considered to be the simpler and more accurate. Both involve the aspiration of air through the sample and its evaporation from a flask. The oxidation test recently standardised by the National Benzol Association[30] is on similar lines to these and is regarded as an alternative to the acid washing test.

Except for the foregoing, comparatively little work has been published during 1932 dealing with the examination of motor fuels. The analysis of "doped" petrols has been the subject of two publications—one on the determination of lead tetramethyl,[31] and the other on the rapid detection of iron carbonyl,[32] using a photo-chemical method. Birch and Scott[33] have suggested a

[24] *Oil & Gas J.*, 1932, **31** (6), 13; *J. Inst. Petr. Techn.*, 1932, **18**, 363A.
[25] Ramsay, *Ind. Eng. Chem.*, 1932, **24**, 539; *J. Inst. Petr. Techn.*, 1932, **18**, 251A.
[26] Aldrich and Robie, *J.S.A.E.*, 1932, **30**, 198; *J. Inst. Petr. Techn.*, 1932, **18**, 251A.
[27] Bridgeman, *Oil & Gas J.*, 9.6.32, **31** (3), 55; *J. Inst. Petr. Techn.*, 1932, **18**, 301A.
[28] Ward, *Oil & Gas J.*, 11.8.32, **31** (12), 14; *J. Inst. Petr. Techn.*, 1932, **18**, 406A.
[29] Haim, *Brenn.-Chem.*, 1932, **13**, 128; *J. Inst. Petr. Techn.*, 1932, **18**, 252A.
[30] Hoffert and Claxton, *Gas Wld.*, 1932, **97**, 560; *J. Inst. Petr. Techn.*, 1933, **19**, 22A.
[31] Baldeschwieler, *Ind. Eng. Chem. Anal.*, 1932, **4**, 101; *J. Inst. Petr. Techn.*, 1932, **18**, 107A.
[32] Kiemstedt, *Erdöl u. Teer*, 1932, **8**, 253; *J. Inst. Petr. Techn.*, 1932, **18**, 253A.
[33] Birch and Scott, *Ind. Eng. Chem.*, 1932, **24**, 49; *J. Inst. Petr. Techn.*, 1932, **18**, 103A.

method for identifying diolefines, and possibly even for estimating them in cracked distillates. The method depends on the formation of acid anhydrides from diolefines by the addition of maleic anhydride. Nunn[34] has shown that, provided the cracking charge is constant with regard to base, the aniline test may be used to evaluate anti-knock value of cracked gasolines. In an attempt to satisfy the demand for the more accurate determination of water content of alcohol fuels, a method has been published[35] which depends on the evolution of hydrogen from calcium hydroxide. Marx[36] has correlated the maximum percentage of carbon dioxide that may be attained when the fuel is completely burned, with A. P. I. gravity and percentage of hydrogen in the fuel.

Sulphur.

A review of the literature has shown that there has been what might almost be called a revival of interest in the determination of sulphur and its compounds. For instance, a method has been described[37] for the determination of elementary sulphur as mercury sulphide, while another[38] consists of a modification of the Halphen colorimetric procedure. Lieber and Rosen[39] have published an improved method for total sulphur, involving the use of a modified Drehschmidt type of apparatus, and two acidmetric methods have been described[40] for the determination of alkyl mercaptans in material containing no unsaturated hydrocarbons. One is an iodometric and the other a mercuric chloride method. Methods of determination have been described by Givaudon,[41] who includes the Grote method, together with one for estimating dissolved hydrogen sulphide in oils. Of interest also in the latter connection is a paper by Wright and Maass,[42] who have determined the vapour density of hydrogen sulphide over a range of temperatures and pressures. Details have been given[43] of a number of modifications

[34] Nunn, *Refiner*, 1932, **11**, 434; *J. Inst. Petr. Techn.*, 1932, **18**, 381A.
[35] Broche and Scheer, *Brenn.-Chem.*, 1932, **13**, 281; *J. Inst. Petr. Techn.*, 1932, **18**, 361A.
[36] Marx, *Refiner*, 1932, **11**, 50; *J. Inst. Petr. Techn.*, 1932, **18**, 141A.
[37] Kiemstedt, *Brenn.-Chem.*, 1932, **13**, 310; *J. Inst. Petr. Techn.*, 1932, **18**, 407A.
[38] Thornton and Latta, *Ind. Eng. Chem. Anal.*, 1932, **4**, 441; *J. Inst. Petr. Techn.*, 1932, **18**, 479A.
[39] Lieber and Rosen, *Ind. Eng. Chem. Anal.*, 1932, **4**, 90; *J. Inst. Petr. Techn.*, 1932, **18**, 106A.
[40] Sampey and Reid, *J.A.C.S.*, 1932, **54**, 3404; *J. Inst. Petr. Techn.*, 1932, **18**, 403A.
[41] Givaudon, *Rev. Petr.*, 1932, (485), 892; *J. Inst. Petr. Techn.*, 1932, **18**, 364A.
[42] Wright and Maass, *Canad. J. Res.*, 1931, **5**, 442; *J. Inst. Petr. Techn.*, 1932, **18**, 32A.
[43] Clacton, Hancock and Hoffert, *Gas J.*, 1932, **199**, 94; *J. Inst. Petr. Techn.*, 1932, **18**, 363A.

in the apparatus and procedure for the determination of sulphur in benzoles in a publication of the Standardization of Tar Products Tests Committee. The carbon disulphide content of benzoles has received attention from Callan, Henderson and Stafford,[44] who describe a colorimetric method for its determination using a dilute solution of a copper salt. A quick corrosion test for casing-head gasoline has been described by Trusty,[45] who uses the reaction of the fuel with mercury to indicate whether or not it is necessary to apply the A. S. T. M. corrosion test.

Gas Oil.

From the point of view of the publication of analytical methods, gas oil has received little attention during the past year in spite of its importance as a high grade Diesel fuel, but a paper by Holmes[46] in connection with the evaluation of the carburetting values of gas oils, is worthy of attention. Here, a dispersion method is used, the dispersion being the difference in the refractive indices of the oil for the C. and F. lines of the solar spectrum at 100° F. The gasification value is calculated from an equation involving the specific gravity, the dispersion and the average boiling point.

Lubricating Oil.

Last year's publications dealing with the examination of lubricants have been of a very diverse nature, but even a cursory review shows that the determination of viscosity still commands a considerable amount of attention. It is for this reason that it has been thought suitable to deal with the question of viscosity apart from this section on lubricating oil.

The results of over two years' work on standardization have been published by the Lubrication Committee of the German Society for Testing Materials,[47] definitions of terms and modifications of tests being included. The D.V.M. Technical Sub-Committee[48] has carried out tests on several flash point apparatus—the Schöter, two forms of the German railway apparatus and the Marcusson. Conventional values were best obtained with the last, which has accordingly been proposed as standard. The survey carried out by the Lubricants Research Sub-Committee of the S.A.E. has been summarised,[49] and special machines for the estimation of load

[44] Callan, Henderson and Stafford, *J.S.C.I.*, 1932, **51**, 193T; *J. Inst. Petr. Techn.*, 1932, **18**, 281A.
[45] Trusty, *Ind. Eng. Chem. Anal.*, 1932, **4**, 33; *J. Inst. Petr. Techn.*, 1932, **18**, 105A.
[46] Holmes, *Ind. Eng. Chem.*, 1932, **24**, 325; *J. Inst. Petr. Techn.*, 1932, **18**, 171A.
[47] *Erdöl u. Teer*, 1932, **8**, 203; *J. Inst. Petr. Techn.*, 1932, **18**, 234A.
[48] *Erdöl u. Teer*, 1932, **8**, 398; *J. Inst. Petr. Techn.*, 1932, **18**, 408A.
[49] *Oil & Gas J.*, 1932, **30** (52), 18; *J. Inst. Petr. Techn.*, 1932, **18**, 259A.

carrying capacity described. Future work on the rating of pressure lubricants is to be carried on by the Bureau of Standards. Tests necessary for the examination of transformer and switch oils have been detailed by the Italian Electro-Technical Association.[50] and in view of the fact that normal transformer tests give only a measure of initial deterioration, the A.E.G.[51] has developed tests involving the use of a specially constructed transformer over periods of 1000–7000 hours. In a study of the changes in physical and electrical properties of a mineral insulating oil heated in contact with air, Race[52] concludes that the major proportion of the non-volatile products containing polar groups cannot be detected by the acid number test and emphasises the value of oil spreading movement. As sulphuric acid is considered to be unsuitable for the examination of high boiling mineral oil, a method[53] has been worked out which involves the determination of molecular weight, specific refraction and aniline point. Nottage,[54] on the other hand, has assayed oils by fractionation with acetone, the fractions being studied by the friction temperature method. The potentiometric titration of acidity has been examined,[55] the platinum-carbon electrode being shown to possess distinct advantages over others, and Galle and Böhm[56] have attempted to modify the rapid iodine number of Margosches in order to make it applicable to the determination of stability of lubricating oils.

The existing methods for determining the characteristics of the mineral oil constituents of greases have been reviewed,[57] and a new method proposed, which is applicable to materials known to contain oleic, stearic and/or palmitic acids. The solubilities of oil and wax in organic solvents have been examined,[58] and as a result, a general equation has been developed for wax solubility. A gravity index for lubricating oils has been evolved[59] for the

[50] *Olii. Min.*, 1932, **12**, 50, 65; *J. Inst. Petr. Techn.*, 1932, **18**, 308A.
[51] Typke, *Erdöl u. Teer*, 1932, **8**, 170, 186; *J. Inst. Petr. Techn.*, 1932, **18**, 214A.
[52] Race, *J. Phys. Chem.*, 1932, **36**, 1928; *J. Inst. Petr. Techn.*, 1932, **18**, 343A.
[53] Vlugter, Waterman and Van Westen, *J. Inst. Petr. Techn.*, 1932, **18**, 735.
[54] Nottage, *J. Inst. Petr. Techn.*, 1932, **18**, 943.
[55] Ralston, Fellows and Wyatt, *Ind. Eng. Chem. Anal.*, 1932, **4**, 109; *J. Inst. Petr. Techn.*, 1932, **18**, 107A.
[56] Galle and Böhm, *Erdöl u. Teer*, 1932, **8**, 76; *J. Inst. Petr. Techn.*, 1932, **18**, 140A.
[57] Foster, *Nat. Petr. News*, 9.3.32, **24** (10), 35; 16.3.32, **24** (11), 33; *J. Inst. Petr. Techn.*, 1932, **18**, 231A.
[58] Poole and Mangelsdorf, *Ind. Eng. Chem.*, 1932, **24**, 1215; *J. Inst. Petr. Techn.*, 1933, **19**, 16A.
[59] McCluer and Fenske, *Ind. Eng. Chem.*, 1932, **24**, 1371; *J. Inst. Petr. Techn.*, 1933, **19**, 23A.

classification of oils as regards their base, and an alignment chart[60] has been prepared to facilitate the calculation of the flash points of known mixtures of lubricating oils. Of very considerable interest is the work of Wade and Foster,[61] who have compared the physical and chemical constants of unused oils with those of oils used in an engine running under standardised conditions. Mention should be made of an automatic Cleveland flash tester with a capacity of five cups,[62] and of a Pensky-Marteus apparatus[63] fitted with a conical inner casing so that small quantities of oil can be tested accurately and rapidly. Two types of surface tension meter have been described by Grant,[64] in which the tension is balanced in one case by gravity and in the other by the elastic torque in a wire. Details of an apparatus for the continuous extraction of oils by liquid sulphur dioxide have been given by Van Dyck,[65] and a description[66] has been given of a machine for determining coefficients of friction. In the latter connection, Sperry and Cammen[67] have advanced a controversial new theory in explanation of the action of a lubricant in the boundary lubrication of a bearing and have developed an ingenious machine consisting essentially of a gyroscopically mounted rotor from which layers of oil are removed by suitable means. To conclude this section, mention should be made of the work of Woog, Ganster and Coulon,[68] who have examined the phase relations of mineral oils at low temperatures and have shown that the setting point depends on the initial temperature of the bath used for warming up from the cold, and that variations in setting points are governed by the previous history of the oil.

Viscometry.

It will be seen from the following that much of the recent work on viscometry has centred around methods for obtaining numerical values for the " viscous-stabilities " of lubricants.

---

[60] Davis, *Oil & Gas J.*, 14.7.32, **31** (8), 38; *J. Inst. Petr. Techn.*, 1932, **18**, 361A.

[61] Wade and Foster, *U.S. Bur. Mines Tech. Paper* 500, 1931; *J. Inst. Petr. Techn.*, 1932, **18**, 123A.

[62] Texas Co., *Ind. Eng. Chem. Anal.*, 1932, **4**, 209; *J. Inst. Petr. Techn.*, 1932, **18**, 233A.

[63] E.P. 364,328; *J. Inst. Petr. Techn.*, 1932, **18**, 109A.

[64] Grant, *J. Sci. Instr.*, 1932, **9**, 108; *J. Inst. Petr. Techn.*, 1932, **18**, 188A.

[65] Van Dyck, *Petr. Z.*, 24.2.32, **28** (8), 7; *J. Inst. Petr. Techn.*, 1932, **18**, 141A.

[66] *Nat. Petr. News*, 1.6.32, **24** (22), 42; *J. Inst. Petr. Techn.*, 1932, **18**, 323A.

[67] *Nat. Petr. News*, 29.6.32, **24** (26), 30; *J. Inst. Petr. Techn.*, 1932, **18**, 408A.

[68] Woog, Gangster and Coulon, *Ann. des Comb. Liq.*, 1932, **7**, 279; *J. Inst. Petr. Techn.*, 1932, **18**, 450A.

In order to classify lubricating oils according to their rate of change of viscosity with change of temperature, an alternative scheme[69] to those of Dean and Davis and Barnard has been devised. In the same connection, it is interesting to note that Bandte,[70] in his work on carbon formation, has concluded that there is a relation between viscosity index and carbon formation in engines. Again, dealing with the same subject, Davis, Lapeyrouse and Dean[71] have given a compilation of the more useful data and charts on viscosity index, while a study has been made[72] of the relationship between mole. fraction and absolute viscosities of blended oils, a method being suggested for predicting the viscosity of blended oils from their mean molecular weights.

In view of the great practical importance of viscosity measurements at high temperatures, it has been proposed[73] to estimate viscosities of lubricating oils in dilute solutions, the expression of results being as molecular or preferably specific viscosities. Viscosities of diluted and undiluted mineral and fatty oils have been determined,[74] using a modified Dallwitz-Wegener viscometer. Ubbelohde[75] has prepared conversion tables for the better known types of viscometers, the system used involving the conversion of the data into absolute units.

With regard to road tars, Barr and Thorogood[76] have dealt comprehensively with the characteristics of the B.R.T.A. instrument (a modification of the Redwood), and of the Hutchinson tar tester. Both instruments are specified in B.S.I. specification 176, 1930 (Road Tars 1 and 2). A modified Ostwald viscometer for volatile and hydroscopic liquids has been described,[77] with which determinations can be made with the apparatus entirely enclosed, without rubber tubing or greased joints. A "Ball Test "[78] has been devised for testing the low-temperature character-

[69] Larson and Schwaderer, *Nat. Petr. News*, 13.1.32, **24** (2), 26; *J. Inst. Petr. Techn.*, 1932, **18**, 123A.
[70] Bandte, *Erdöl u. Teer*, 1932, **8**, 10; *J. Inst. Petr. Techn.*, 1932, **18**, 124A.
[71] Davis, Lapeyrouse and Dean, *Oil & Gas J.*, 31.3.32, **30** (46), 92; *J. Inst. Petr. Techn.*, 1932, **18**, 212A.
[72] Epperson and Dunlap, *Ind. Eng. Chem.*, 1932, **24**, 1369; *J. Inst. Petr. Techn.*, 1933, **19**, 24A.
[73] Tausz and Rabl. *Erdöl u. Teer*, 1932, **8**, 396; *J. Inst. Petr. Techn.*, 1932, **18**, 406A.
[74] Tausz and Mellner, *Petr. Z.*, 1932, **28** (45), 1; *J. Inst. Petr. Techn.*, 1933, **19**, 18A.
[75] Ubbelohde, *Erdöl u. Teer*, 1932, **8**, 46; *Petr. Times*, 1932, **27**, 100; *J. Inst. Petr. Techn.*, 1932, **18**, 140A.
[76] Barr and Thorogood, *J.S.C.I.*, 1932, **51**, 381; *J. Inst. Petr. Techn.*, 1933, **19**, 17A.
[77] Andrade and Spells, *J. Sci. Instr.*, 1932, **9**, 316; *J. Inst. Petr. Techn.*, 1932, **18**, 449A.
[78] Bittner, *Nat. Petr. News*, 19.10.32, **24** (42), 31; *J. Inst. Petr. Techn.*, 1932, **18**, 479A.

istics of oils and greases. The test consists of measuring the force required to pull a steel ball at a constant rate through a cup containing the chilled sample. Arveson[79] has developed a grease viscometer which comprises a constant speed piston passing into a cylinder containing the sample, the latter being forced downwards against mercury and out through a capillary. A continuous double-orifice type of viscometer has been patented,[80] and a description has been published[81] of a high precision, electrically heated and controlled water bath, while a filling device for upward-flow viscometers is dealt with by Barraston.[82]

Asphaltic-Bitumen.

The ever expanding uses of asphaltic-bitumen, whether for road-making, for electrical insulation or for paints, etc., are constantly showing the necessity for the development of new analytical methods. Although to the writer's knowledge much valuable work has been and is being carried out, relatively few publications of value have appeared dealing with the more critical examination and testing of this type of material.

Maas[83] has described certain analytical methods at length, with particular attention to the estimation of paraffin content by a combination of acid treatment and " bleaching." Muller and Wandyez[84] have also put forward a new method for the estimation of paraffin, in which, after the removal of asphaltenes, the wax is precipitated from pyridine solution at 0° C. Evans[85] has studied the physical properties of mixtures of bitumen with finely-divided mineral matter, using, besides the normal tests, an apparatus for measuring tensile strength based on the tensometer described by Abrahams. The Rothamsted pachimeter,[86] although primarily designed for soils, has been suggested as being suitable for the measurement of shearing strength, plasticity, viscosity and elasticity of asphaltic bitumens. Corrosion tests on asphalts have been described,[87] in which, after being applied

[79] Arveson, *Oil & Gas J.*, 31.3.32, **30** (46), 96 ; *J. Inst. Petr. Techn.*, 1932, **18**, 231A.

[80] Albersheim and Konheim, E.P. 376,253 ; *J. Inst. Petr. Techn.*, 1932, **18**, 365A.

[81] Ferguson, Lente and Hitchens, *Ind. Eng. Chem. Anal.*, 1932, **4**, 218 ; *J. Inst. Petr. Techn.*, 1932, **18**, 233A.

[82] Barraston, *Analyst*, 1932, **57**, 309 ; *J. Inst. Petr. Techn.*, 1932, **18**, 234A.

[83] Maass, *Petr. Z.*, 25.5.32, **28** (21), 1 ; *J. Inst. Petr. Techn.*, 1932, **18**, 362A.

[84] Müller and Wandycz, *Asphalt u. Teer*, 1932, (36) ; *J. Inst. Petr. Techn.*, 1932, **18**, 450A.

[85] Evans, *J. Inst. Petr. Techn.*, 1932, **18**, 957.

[86] Schofield and Blair, *J.S.C.I.*, 1932, **51**, 205 ; *J. Inst. Petr. Techn.*, 1932, **18**, 141A.

[87] Schwarz, *Petr. Z.*, 22.6.32, **28** (25) ; *Asphalt u. Strassenbau*, **4**, 2 ; *J. Inst. Petr. Techn.*, 1932, **18**, 363A.

to metal strips and subjected to corrosive agents, the samples are melted on to glass and examined under the microscope. The quantitative identification of rubber in rubber bitumen mixtures is the subject of a paper[88] by van Heurn and Begheyn, while another,[89] dealing with the estimation of asphaltic bitumen in tar, gives a method based on the difference in critical surface tension shown by asphalt and tar and the varying miscibilities of the oily media of both systems. Interfacial tension between asphaltic materials and various aqueous solutions has been studied[90] by means of the du Noüy interfacial tensiometer method, and Wolf[91] has given a description of a new type of asphalt penetrometer. The instrument is operated on normal principles, but the needle is replaced by a stout rod, greater loads and longer contact periods being used.

The satisfactory examination of bitumen emulsions presents difficulties even greater than those experienced with asphaltic-bitumen itself, so that it is not surprising that there is a paucity of recent publications in this connection.

Pages and Houlnik[92] have surveyed methods of test for emulsions and described in particular those for water and bitumen content, total and free alkalinity, sedimentation, stability and breakdown index in contact with stone. With regard to the last item, a method has been published[93] which consists of mixing known quantities of emulsion and stone and determining the weight of bitumen obtained on 100 gms. of stone, this being known as the "break-down value." A new method of separating emulsifiers from bitumen by means of suitably prepared cotton flannel has been described by Neubronner,[94] and a demulsification test is stated by Myer[95] to consist of treatment of the emulsion with calcium chloride solution followed by passage through a sieve for the removal of water. Mention should lastly be made of the work of Vellinger and Flavigny[96] dealing with the physico-chemical

[88] Van Heura and Begheyn, *India Rubber J.*, 1931, **81** (26), 15.
[89] Nellensteyn and Kuipers, *Bitumen*, 1932, **2**, 123; *J. Inst. Petr. Techn.*, 1932, **18**, 408A.
[90] Traxler and Pittman, *Ind. Eng. Chem.*, 1932, **24**, 1003; *J. Inst. Petr. Techn.*, 1932, **18**, 386A.
[91] Wolf, *J. Sci. Instr.*, 1932, **9**, 22; *J. Inst. Petr. Techn.*, 1932, **18**, 91A.
[92] Pages and Houlnik, *Olii. Min.*, 1932, **12**, 118; *J. Inst. Petr. Techn.*, 1932, **18**, 451A.
[93] Weber and Bechler, *Asphalt u. Teer*, 1932, **32**, 45; *J. Inst. Petr. Techn.*, 1932, **18**, 265A.
[94] Neubronner, *Chem. Z.*, 1932, **56**, 429; *J. Inst. Petr. Techn.*, 1932, **18**, 362A.
[95] Smith, *Ind. Eng. Chem. Anal.*, 1932, **4**, 105; *J. Inst. Petr. Techn.*, 1932, **18**, 107A.
[96] Vellinger and Flavigny, *Ann. des Comb. Liq.*, 1932, **7**, 217; *J. Inst. Petr. Techn.*, 1932, **18**, 433A.

properties of bitumen emulsions, in which it was found that the stability of emulsions is related to the p_H value of the aqueous phase.

Laboratory Distillation.

The development of laboratory atmospheric or vacuum distillation apparatus, whether intended for accurate fractionation analysis or for the duplication of the results of large-scale plant distillation, presents an almost continuous problem. Apparatus and methods developed during 1932 have been very diverse, especially for the batch type of distillation, but except for one instance little has been accomplished in the realm of continuous distillation.

A mathematical treatment of the fractional distillation of ideal mixtures has been given by Stedman,[97] who makes use of the "critical reflux ratio" for any mixtures above which even an infinite column cannot obtain complete separation. A high vacuum apparatus, including a Kjeldahl flask fitted with an internal electric heater, has been used for studying the composition of vapours from binary solutions,[98] and a description[99] has been given of a set of glass rectifying stills and jacketed bubble cap columns suitable for use at pressures from atmospheric down to about 50 mm. For the assay of crude oil, Trusty[100] has given a description of a simple laboratory method, using a 3-litre flask fitted with a 14 in. Hempel column, for light fractions. The column is replaced by an iron "goose-neck" for the gas oil fraction, and by a short ¼ in. pipe for the vacuum distillation of the lubricating oil distillate. In order to evaluate crude oils with regard to octane rating of their motor spirit fractions, a method has been proposed[101] based on a fractional-gravity distillation by means of which the yield and gravity of spirit of any desired end-point may be determined. Podbielniak[102] has described some additions and improvements which have been incorporated in his distillation apparatus. These include the replacement of the silver plating in the vacuum jacket by a highly polished metal reflector, a variety of interchangeable distilling tubes, cooling vessels designed to give maximum condensation with minimum refrigerant, and an automatic device which

[97] Stedman, *Canad. J. Res.*, 1931, **5**, 455; *J. Inst. Petr. Techn.*, 1932, **18**, 32A.

[98] Othver, *Ind. Eng. Chem. Anal.*, 1932, **4**, 232; *J. Inst. Petr. Techn.*, 1932, **18**, 233A.

[99] Bruun and Schicktanz, *Bur. Stand. J. Res.*, 1931, **7**, 851; *J. Inst. Petr. Techn.*, 1932, **18**, 70A.

[100] Trusty, *Petr. Eng.*, 1932, **3** (10), 30; *J. Inst. Petr. Techn.*, 1932, **18**, 360A.

[101] Clay, *Oil & Gas J.*, 21.3.32, **30** (46), 70; *J. Inst. Petr. Techn.*, 1932, **18**, 228A.

[102] Podbielniak, *Oil & Gas J.*, 21.3.32, **30** (46), 68; *J. Inst. Petr. Techn.*, 1932, **18**, 229A.

supplies liquid air for reflux cooling, controls distillation rate, keeps distillation pressure constant and plots the finished distillation curve directly on a chart. The original apparatus is the subject of a patent.[103]

For the purpose of studying the composition and knock rating of straight-run Pennsylvanian gasoline, two packed metal fractionating columns have been developed.[104] Their essential features were adiabatic operation, controlled reflux and high efficiency with large throughput and minimum of liquid hold up.

The lengths of the columns, however, are excessive for the ordinary laboratory. In connection with their work on the influence of fractionation on distribution of sulphur in gasoline, Espach and Rue[105] have described in detail a laboratory pipe still and bubble-cap tower unit. Details have been given of a 50 gallon distillation apparatus fitted with a 20 ft. column[106] and an ingenious apparatus for the automatic periodic determination of final boiling point has been patented.[107]

In connection with the production and study of lubricating oi distillates, Guthrie and Higgins[108] have constructed a 5-litre glass vacuum distillation apparatus consisting of a flask welded to a fractionating column. The flask rests in an electrically-heated metal bath and the column is lagged with two concentric air jackets, the inner one being electrically heated. A description has been given[109] of a fractionating column for use under diminished pressure. It is attached to the reflux head and still by ground glass joints and is electically wound to prevent loss of heat by radiation. Greutert[110] has described a vacuum distillation apparatus involving the use of carbon dioxide for the recovery of an asphaltic bitumen from solutions without impairing its properties to any great extent. Interesting adjuncts to laboratory distillation apparatus are an anti-foam still head for laboratory distillation,[111] an improved McLeod gauge and manometer[112] which will work

[103] E.P. 380,220 ; *J. Inst. Petr. Techn.*, 1932, **18**, 481A.
[104] Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, 1932, **24**, 408 ; *J. Inst. Petr. Techn.*, 1932, **18**, 190A.
[105] Espach and Rue, *U.S. Bur. Mines Tech. Paper* 505 ; *J. Inst. Petr. Techn.*, 1932, **18**, 49A.
[106] Conine, *Oil & Gas J.*, 18.8.32, **31** (13), 13 ; *J. Inst. Petr. Techn.*, 1932, **18**, 409A.
[107] U.S.P. 1,876,364 ; *J. Inst. Petr. Techn.*, 1932, **18**, 452A.
[108] Guthrie and Higgins, *U.S. Bur. Mines Rept. Invest.* 3159 ; *J. Inst. Petr. Techn.*, 1932, **18**, 231A.
[109] Bush and Schwartz, *Ind. Eng. Chem. Anal.*, 1932, **4**, 142 ; *J. Inst. Petr. Techn.*, 1932, **18**, 108A.
[110] Greutert, *J. Inst. Petr. Techn.*, 1932, **18**, 846.
[111] Eddy, *Ind. Eng. Chem. Anal.*, 1932, **4**, 198 ; *J. Inst. Petr. Techn.*, 1932, **18**, 234A.
[112] Booth, *Ind. Eng. Chem. Anal.*, 1932, **4**, 380 ; *J. Inst. Petr. Techn.*, 1932, **18**, 481A.

over a range 760 to 0·00001 mm., and an improved distillation trap[113] for removing fine spray from vapours.

Physical Determinations.

Physical determinations used in the examination of petroleum are invariably of the greatest use to the petroleum engineer, and much of the recent development of refinery engineering is due to a better understanding and use of physical data. Field engineers, and even geologists, are finding it increasingly advantageous to make use of the considerable amount of information now available, for example, in the determination of the life and potential yields of wells and fields. For these reasons, therefore, it has been considered desirable to summarise recent physical work in the following separate section.

With regard to vapour pressure, Felton[114] has examined the technique of the Reid test and suggested certain minor improvements and modifications to the apparatus. The Bat. Petr. Mij. has published[115] their method of vapour pressure determination, which is based on the increase in volume observed when a measured quantity of air is brought into contact with a gasoline and thoroughly saturated with its vapour, the pressure being kept constant. Partial vapour pressures and refractivities have been determined[116] on mixtures of benzene and some of its polar derivatives, and an examination of the thermal properties of petroleum distillates[117] has shown that the P-V-T relationships of petroleum hydrocarbon mixtures are similar in all respects to those of binary mixtures previously examined. Continuing their work on the physical properties of petroleum, Land and Jessel[118] have investigated the total heat and specific heat of a series of fractions of Miri, Persian and Venezuelan crude oils and their relation to other properties. Recent work dealing with specific heats of mineral oils has been reviewed by Kraussold,[119] who describes an electrically-heated calorimeter. An informative paper[120] on the thermal properties of oil fractions has been pub-

[113] West, *Ind. Eng. Chem. Anal.*, 1932, **4**, 445; *J. Inst. Petr. Techn.*, 1932, **18**, 479A.
[114] Felton, *Oil & Gas J.*, 31.3.32, **30** (46), 28; *J. Inst. Petr. Techn.*, 1932, **18**, 229A.
[115] *J. Inst. Petr. Techn.*, 1932, **18**, 716.
[116] Martin and Collie, *J.C.S.*, 1932, **135**, 2658; *J. Inst. Petr. Techn.*, 1933, **19**, 15A.
[117] Bahlke and Kay, *Ind. Eng. Chem.*, 1932, **24**, 291; *J. Inst. Petr. Techn.*, 1932, **18**, 188A.
[118] Lang and Jessel, *J. Inst. Petr. Techn.*, 1932, **18**, 108.
[119] Kraussold, *Petr. Z.*, 20.1.32, **28** (3), 1; *J. Inst. Petr. Techn.*, 1932, **18**, 108A.
[120] Edminster, *Oil & Gas J.*, 25.2.32, **30** (41), 50; *J. Inst. Petr. Techn.*, 1932, **18**, 137A.

lished by Edminster, and another communication[121] has dealt with the heat capacity of organic compounds determined with the aid of a radiation calorimeter. The heat contents of petroleum fractions at elevated temperatures have been investigated,[122] and Rossine[123] has determined the heats of combustion of methyl and ethyl alcohols. The thermodynamic principles involved in the determination of the difference between gross and nett heating values for both constant volume and constant pressure combustion of solid and liquid fuels have been discussed,[124] while a method and apparatus for the determination of the nett heating value of fuels has been patented.[125] A refinement of Zeitfuch's method of determining critical temperatures has been described by Eaton and Porter.[126] The improvement consists in providing means for agitating the oil sample contained in a thin-walled Pyrex tube, while it is being heated to the critical temperature. The boiling points, freezing points and refractive indices of normal paraffins from pentane to dodecane have been determined,[127] and Wright[128] has described a method for the determination of the density of a saturated vapour at the boiling point of the liquid yielding the vapour.

Measurements of thermal expansion on a number of straight-run and cracked motor fuels, benzoles and blends thereof have been made,[129] results showing that the expansions of cracked fuels and benzol blends are systematically greater than the values for straight-run material. Finally, an instrument for measuring the density of liquids under pressure in pipe lines has been patented.[130]

Chemical.

A convenient method for the determination of carbon in organic compounds has been described by Chalmers,[131] who measures the

[121] Spaight, Thomas and Parks, *J. Phys. Chem.*, 1932, **36**, 882; *J. Inst. Petr. Techn.*, 1932, **18**, 139A.
[122] Wier and Eaton, *Ind. Eng. Chem.*, 1932, **24**, 211; *J. Inst. Petr. Techn.*, 1932, **18**, 135A.
[123] Rossini, *Bur. Stand. J. Res.*, 1932, **8**, 119; *J. Inst. Petr. Techn.*, 1932, **18**, 136A.
[124] Lichty and Brown, *Ind. Eng. Chem.*, 1931, **23**, 1419; *J. Inst. Petr. Techn.*, 1932, **18**, 70A.
[125] E.P. 361,271; *J. Inst. Petr. Techn.*, 1932, **18**, 33A.
[126] Eaton and Porter, *Ind. Eng. Chem.*, 1932, **24**, 819; *J. Inst. Petr. Techn.*, 1932, **18**, 322A.
[127] Mair, *Bur. Stand. J. Res.*, 1932, **9**, 457; *J. Inst. Petr. Techn.*, 1932, **18**, 478A.
[128] Wright, *J. Phys. Chem.*, 1932, **36**, 2793; *J. Inst. Petr. Techn.*, 1933, **19**, 15A.
[129] Cragoe and Hill, *Bur. Stand. J. Res.*, 1931, **7**, 1133; *J. Inst. Petr. Techn.*, 1932, **18**, 86A.
[130] E.P. 365,141; *J. Inst. Petr. Techn.*, 1932, **18**, 99A.
[131] Chalmers, *Ind. Eng. Chem. Anal.*, 1932, **4**, 1; *J. Inst. Petr. Techn.*, 1932, **18**, 105A.

increase in pressure due to the evolution of carbon dioxide formed by the action of a mixture of chromic acid anhydride and sulphuric acid on the sample. Pressure change in an isothermal system before and after vaporisation has been utilised by Bratten and Lochte [132] in their micro method of molecular weight determination, while details have been given [133] of a method for the estimation of isopropyl alcohol in ethyl alcohol based on the difference in solubility of caustic soda in the two alcohols.

Geo-Chemical.

Under this heading little has been published during 1932, but the paper of Jones and Wood[134] is worthy of note. In their study of oilfield water analysis, they have studied the benzidine hydrochloride method for the estimation of the sulphate radicle, together with its accuracy and the effect of the presence of calcium and magnesium. In the second part of their paper they have studied the volumetric estimation of calcium in the presence of magnesium.

[132] Bratton and Lachte, *Ind. Eng. Chem. Anal.*, 1932, **4**, 365; *J. Inst. Petr. Techn.*, 1932, **18**, 481A.

[133] Archibald and Beamer, *Ind. Eng. Chem. Anal.*, 1932, **4**, 18; *J. Inst. Petr. Techn.*, 1932, **18**, 105A.

[134] Jones and Wood, *J. Inst. Petr. Techn.*, 1932, **18**, 817.

Standard Methods of Testing Petroleum and Its Products.

By Professor J. S. S. Brame, C.B.E., F.I.C., F.C.S. (Past President), Chairman of the Standardization Committee.

Since the publication of the second edition of "Standard Methods of Testing Petroleum and Its Products" in 1929, the Standardization Committee of the Institution of Petroleum Technologists has had under consideration the revision of, and addition to, the methods of test laid down in that book. The Committee and its sub-committees have received many helpful comments and suggestions and have carried out a considerable amount of research work in order to determine the best procedure to be adopted for a particular test. It is hoped that the result of their labours will be ready for publication as a third edition of the method book early in 1934.

The Committee has enjoyed the continued and cordial co-operation of Committee D-2 of the American Society for Testing Materials and of similar bodies in other countries. The British Standards Institution has also worked in close co-operation with the Committee.

It is not proposed in this short article to deal with the various minor amendments which are under consideration, but a few notes regarding additional tests will be given.

The question of the determination of gum in gasoline has been referred to a special sub-committee who have carried out numerous tests and arrived at a method for the determination of existent gum. The attention of the sub-committee is now directed to devising a satisfactory test for the determination of potential gum.

The importance of the knock-rating of motor fuels is such that a new sub-committee was appointed to study this property and the method of its assessment. Close contact has been established with the C.F.R. Committee in the United States and with various bodies on the Continent. A large amount of experimental work has been involved and there has been a regular exchange of data and comments between the United States and this country. As a result of this work, the C.F.R. engine and the technique of the test (motor method) were adopted by the A.S.T.M. as a tentative standard as from April 1st, 1933, and by this Institution as from May 1st, 1933, and it is hoped that this method, and the expression of knock-rating in terms of octane numbers, will become international.

The conditions under which fuels are burnt in aircraft engines differ considerably from those in motor cars and a panel of the

Knock-Rating Sub-Committee was therefore appointed to consider the conditions which would have to be employed in the test engine when testing such fuels. This panel, which received valuable assistance from the Air Ministry and from the Bristol Aeroplane Company, has now presented its report.

The desirability of a standard test for the tendency to smoke of a kerosine when burned in a lamp led to the formation of a special sub-committee to consider this matter. The basis of such a test was already in existence[1] and its usefulness had been further indicated by Minchin.[2] The apparatus then used, however, was somewhat costly and at the present time a suitable lamp is being constructed which it is anticipated will meet the requirements of this test.

Considerable experimental work in connection with the development of lubricating oil tests has been carried out by the members of the Lubricating Oil Sub-Committee. One problem of importance concerned the stability of turbine oils, and a preliminary series of tests was carried out at the request of the British Standards Institution. It was concluded that the usual stability tests were not entirely satisfactory and some improved form of test would have to be provided. A panel composed of members of the Lubricating Oil Sub-Committee and of the British Standards Institution has now been created to study this matter.

The need for new authentic tables for the conversion of Redwood viscosities to kinematic viscosities has been recognised for some years past. This matter has been discussed with the Director of the National Physical Laboratory, who has expressed his willingness to undertake the investigation and the compilation of the results, and a grant of £100 from the Research Fund of the Institution has been made to cover the cost of the work at the National Physical Laboratory.

The need for standard tests for lubricating greases has been before the Committee on several occasions and a series of tests has been drawn up by a special panel and now awaits further consideration.

The determination of the spontaneous ignition temperature of fuel oils has been the subject of many technical articles, and an important contribution to the literature was made by the symposium organised by the members of the panel appointed to deal with this subject.[3] This panel has now been strengthened by the addition

[1] Kewley and Jackson, *J. Inst. Petr. Techn.*, 1927, **13**, 372.
[2] *J. Inst. Petr. Techn.*, 1931, **17**, 102.
[3] *J. Inst. Petr. Techn.*, 1932, **18**, 533–594.

of members of the British Standards Institution's Diesel Fuel Committee, and is considering all tests pertinent to Diesel fuels.

The extending use of bitumen and asphalt for road work, electrical insulation, etc., has made it necessary for careful consideration to be given to the tests to be applied to determine the suitability of such products for these purposes, and the sub-committee concerned has the matter before them.

Much consideration has been given to the possibility of standardising a method for the determination of oil in paraffin wax or scale, but no method capable of giving general satisfaction has been evolved. While the desirability of an accurate method is acknowledged, it is realised that the effect of oil upon the physical properties of wax is dependent, not only upon the proportion of oil, but also upon its character. While it is recognised that physical tests, other than those standardized, have been employed in the industry, it would appear that none of them is in such general use as to command recognition as a standard.

The conversion of petroleum weights to measures and vice versa has been the subject of much controversy and it was felt that this was a matter which could well be taken up by the Institution of Petroleum Technologists through its Standardization Committee. An additional sub-committee was therefore formed, and after a great deal of work, in which they had the valued co-operation of the Standards Department of the Board of Trade, the National Physical Laboratory, and the United States Bureau of Standards an interim report was presented. It was recognised that this report would be of the greatest value to the industry, and it was therefore published in 1932 as "Measurement of Oil in Bulk. Part I. Standard Weights and Measures." In this book, the derivation of the various units is outlined and a very full table of inter-related units given, which includes a series of contracted ratios which are recommended for general use. As the work of the sub-committee progresses other parts of the book will appear on related subjects.

In connection with the testing of petroleum and its products, it is hoped that the World Petroleum Congress will afford an opportunity of agreement being reached on some tests which are the subject of much discussion. One of the most important features of the Congress will be the Session on International Standardization, and it is confidently anticipated that this, taken in conjunction with the meeting of Committee 28 of the International Standards Association, which is being held in London during the Congress, will lead to the formulation of a scheme by which it will be possible to obtain international agreement on at least the most important tests applicable to petroleum products.

Chemistry of Petroleum.

By D. A. Howes, Ph.D., B.Sc. (Associate Member).

Crude Petroleum.

The origin of crude petroleum continues as a subject of much speculation. Rakusin[1] has shown by experiment that abietic acid, phytosterol chloresterol and betulin yield a wide range of hydrocarbons when distilled with aluminium chloride. These hydrocarbons are optically active in their higher fractions, and a similar mechanism has been suggested for the formation of the optically active constituents of petroleum from plant substances.

Similar work has been reported by Freund,[2] who has obtained hydrocarbons resembling petroleum from turpentine oil by treatment with the same reagent. Using a turpentine oil of which the main constituent was l-pinene, he obtained r-rotatory decomposition products, but fractional distillation of these products gave a series of fractions which with increasing boiling point yielded first r-rotatory, then l-rotatory and finally r-rotatory compounds, a property also of some Java petroleums. Freund concludes that terpenes are present in the mother substance of petroleum.

Berl[3] has developed the theory that humus coal, petroleum and asphalt, which belong fundamentally to the same class of substances, are formed from cellulose. The presence of optically active compounds in petroleum has been explained by assuming that cellulose can give similar substances on decomposition.

According to Von Braun,[4] there is considerable evidence that the nitrogen compounds found in petroleum owe their origin to protein bodies. Thus protein rich substances such as cotton-seed meal yield, on distillation with nitrogen free mineral oil, basic materials which show great similarity to those obtained from petroleum. Galician petroleum has been found to contain o-, m- and para cresol, β naphthol and several xylenols, but not phenol.[4]

The naphthenic acid contents of crude oils continue to attract attention. According to Von Braun,[5,6] the North Germany, Rumanian, Californian and Texas crude oil naphthenic acids are of the general formula $C_nH_{2n-2}O_2$ in their lower members and $C_nH_{2n-4}O_2$ in the higher members—*i.e.*, the compounds are

[1] Rakusin, *Petr. Z.*, 20.1.32, **28** (3), 9–12; *J. Inst. Petr. Techn.*, 1932, **18**, 136A.
[2] Freund, *Petr. Z.*, 14.9.32, **28** (37), 1–8; *J. Inst. Petr. Techn.*, 1932, **18**, 449A.
[3] Berl, *Petr. Z.*, 17.8.32, **28** (33), 1–10; *J. Inst. Petr. Techn.*, 1932, **18**, 374A.
[4] Von Braun, *Z. angew. Chem.*, 1931, **44**, 661–676; *Nat. Petr. News*, 24.2.32, **24** (8), 28–32; *J. Inst. Petr. Techn.*, 1932, **18**, 184A.
[5] Von Braun, *Ann.*, 1931, **490**, 100–179.
[6] Von Braun, *Z. angew. Chem.*, 1931, **44**, 661–664.

types while the Galician acids are monocyclic far above C_{18}. The presence of $C_6H_{11}\cdot CH_2\cdot CH_2\cdot COOH$ was established by the preparation from it of succinic acid. The formation of naphthenic acids has been considered by Petrov and Ivanov,[7] who have cracked oleic acid in the presence of water and alumina and obtained hydrocarbons of octanaphthene and nonanaphthene structure. Oxy and carboxy acids of monocyclic naphthene type were obtained by oxidising Emba gas oil at 90°–100° C. in the presence of catalysts. The naphthenic acid contents of fractions monocyclic and bicyclic acids respectively. The molecular weight range of 200–210 is stated to be the dividing line between the two of Balachany crude have been stated to be :—Cylinder oil 0·4 per cent., low gravity kerosine 0·6 per cent., and fraction sp. gr. 0·86–0·9 (*i.e.*, heavy kerosine to spindle oil), 2·0 per cent.[8] Information has also been published concerning the acids present in Baku petroleum.[9] The lower boiling fractions of the acids contain almost exclusively aliphatic acids, among which isoamylacetic and diethylpropionic acids were definitely identified. Cyclic acids start appearing with the fraction b.p. 215° C., the proportion increasing with the boiling point until above 260° C. there are little or no aliphatic acids. The aliphatic acids in the lower boiling fractions are mainly primary and (contrary to the findings of Von Braun) the cyclic acids present in these same fractions are mostly secondary ; the presence of tertiary acids has not yet been definitely proved. A method of fractional precipitation of the salts of cadmium and a few other heavy metals has been developed in this investigation. The naphthenic acids of Grabownica and Western Galicia crude oils have been investigated by Pilat and Reyman,[10] while the well-known Charichkov test for naphthenic acids has been shown capable of detecting concentrations as low as 0·1 per cent. Phenols do not interfere with this test, but asphalt does.[11] Naphthenic acids have been found to occur in small quantities (0·0013 per cent.—0·47 per cent.) in some oil well waters,[12] while the salts of these acids are considered to have considerable commercial applications in paints and pigments.[13]

---

[7] Petrov and Ivanov, *J.A.C.S.*, 1932, **54**, 239 ; *J. Inst. Petr. Techn.*, 1932, **18**, 104A.

[8] Schmitz, *Erdöl u. Teer*, 1932, **8**, 27–29, 44–46 ; *J. Inst. Petr. Techn.*, 1932, **18**, 128A.

[9] Chichibabin, Chirikov, Katznelson, Koryagin and Chelintzer, *Chim. et Ind.*, Spec. No., March, 1932, 306–318 ; *Chem. Abs.*, 1932, **26**, 3654.

[10] Pilat and Reyman, *Ann.*, 1932, **499**, 76–83 ; *J. Inst. Petr. Techn.*, 1932, **18**, 478A.

[11] Luft, *Petr. Z.*, 15.6.32, **28** (24), 16–17 ; *Chem. Abs.*, 1932, **26**, 4706 ; *J. Inst. Petr. Techn.*, 1932, **18**, 360A.

[12] Reisner, *Neft. Khoz.*, 1931 (11–12), 127–128 ; *Chem. Abs.*, 1932, **26**, 2308.

[13] *Chem. Trade J.*, 1932, **91**, 238 ; *J. Inst. Petr. Techn.*, 1932, **18**, 437A.

The metallic constituents of crude petroleums have been studied by Shirey,[14] who concludes that there is a loose quantitative relationship between the vanadium and nickel contents, and that while nickel occurs to some extent in the ash from all crudes, vanadium appears to associate itself more strictly with asphaltic crudes. With regard to other constituents, little or no regularity has been found. The presence of mineral constituents in oil may be due: (*a*) to emulsified sub-surface waters; (*b*) to the true solution of the minerals in the oil; or (*c*) to the formation of chemical compounds between the metals and the organic constituents of the oil. Of these the first hypothesis is not probable, while asphalt may dissolve or react with metallic compounds. The analysis did not reveal the common occurrence of metals in sufficient amount to make petroleum ash of interest as a source of rarer metals.

Crude petroleums have also been found to contain molybdenum by Meulin.[14a]. Persian crude contained 0·013 mgm. per kilo and Mexican crude 5·55 mgm. per kilo, but no molybdenum was detected in a sample of sea water.

Shales and Shale Oils continue to be examined by Kogerman. Estonian oil shale, "Kukkersite," has been found to be, from the colloid chemistry point of view, of the "irreversible coagulum type," while the organic matter of the shale may be regarded as a highly polymerised "resinic substance" mixed with calcium salts of fatty acids. It is insoluble in all ordinary organic solvents, and can be depolymerised and decomposed only by the action of heat. The four main groups of organic substances which occur in coal tar and petroleum—*i.e.*, phenols, acids, bases and neutral substances, have been separated from the shale oil. Of these, the acids are mainly fatty acids, the bases belong to the derivatives of pyridine and quinoline, while in the lighter hydrocarbon fractions paraffins predominate. The role of plankton-organisms in the formation of oil shale deposits is considered to be of more importance than has been recognised.[15] The physical properties of Estonian shale oils have recently been determined,[16] while the existence of optical activity in fractions of Autun shale oil has led Boulzaquet and Freiss[17] to believe in related origins for shales and petroleum. The chemistry of the conversion of algæ into

[14] Shirey, *Ind. Eng. Chem.*, 1931, **23**, 1151–1153; *J. Inst. Petr. Techn.*, 1932, **18**, 4A.

[14a] Meulen, *Nature*, 1932, **130**, 966.

[15] Kogerman, *Arch. Natur. Estlands*, 1 *Ser. Geol. Chem. Phys.*, 1931, **10** (2), 61–141; *Chem. Abs.*, 1932, **26**, 1423.

[16] Kogerman and Koll, *Sitzl. Natur.-Ges. Univ. Tartu*, 1931, **37** (3–4), 216-232; *Chem. Abs.*, 1932, **26**, 287.

[17] Boulzaquet and Friess, *Ann. Des. Comb. Liq.*, 1932, **7**, 55–58; *J. Inst. Petr. Techn.*, 1932, **18**, 360A.

bitumen and petroleum has been dealt with at length by Hackford,[18] who has developed a new theory named " the carbohydrate theory of the origin of oil," and shown that oil and bitumen are products resultant upon the prolonged acid hydrolysis of algæ or its decomposition products—*e.g.*, the sugars and calcium salts of the ethereal sulphonic esters, at low temperatures.

Oil Field Waters at Grozny have been found to be nearly 100 times as rich in radium as the Heidelberg radium hot springs. It has been found that certain aquatic plants withdraw radium from sea water and store it up, but this fact cannot explain its presence in oil brines, since the half life period of radium is less than 1580 years. Either the petroleum forming organisms stored up thorium or uranium I., or else the radium was taken up by the oil field waters only a short time ago.[19] Economic production of iodine from the oil well waters in the Dutch East Indies has been reported,[20] and an analysis of the waters from the Bulu well near Surabaya has shown these to contain 0·153 grams Mg. I_2 per litre. The analysis of oil field waters has been recently considered by Jones and Wood.[21]

The Preparation of Pure Hydrocarbons has been carried out by Wilkinson,[22] who has synthesised the olefines up to nonene-1 and determined their main physical properties, and by Schmitt and Boord,[23] who have prepared ten of the thirteen structurally possible hexenes, including those hitherto unknown. Mair[24] has effected the synthesis and purification of the normal paraffin hydrocarbons from pentane to dodecane, pure octene-1 has been prepared by Waterman and Te Nuyl,[25] pure methane and ethane by MacGilliveray[26] and 2, 11 dimethyldodecane and 2, 19 dimethylicosane have been synthesised by Landa and Kejvan.[27]

Work continues at the Bureau of Standards on the isolation of pure hydrocarbons from the light distillates of a crude petroleum from the South Ponca Field of Oklahoma, and methyl-

[18] Hackford, *J. Inst. Petr. Techn.*, 1932, **18**, 74.
[19] Saloman-Calni, *Intern. Z. Bohrtech., Erdölbergbau u. Geol.*, 1931, **39** (12), 93–94; *Chem. Abs.*, 1932, **26**, 287.
[20] *Chem. Trade J.*, 1931, **90**, 451; *J. Inst. Petr. Techn.*, 1932, **18**, 267A.
[21] Jones and Wood, *J. Inst. Petr. Techn.*, 1932, **18**, 817.
[22] Wilkinson, *J.C.S.*, **134**, 3057.
[23] Schmidt and Boord, *J.A.C.S.*, 1932, **54**, 751; *J. Inst. Petr. Techn.*, 1932, **18**, 104A.
[24] Mair, *Bur. Stand. J. Res.*, 1932, **9**, 457–472; *J. Inst. Petr. Techn.*, 1932, **18**, 478A.
[25] Waterman and Te Nuyl, *Rec. trav. Chim.*, 1932, **51**, 533–537.
[26] McGilliveray, *J.C.S.*, 1932, **135**, 941–952; *J. Inst. Petr. Techn.*, 1932, **18**, 188A.
[27] Landa and Kejvan, *Coll. Czechoslav. Chem. Comm.*, 1931, **3**, 367–376; *Chem. Abs.*, 1932, **26**, 77.

cyclopentane,[28] normal nonane,[29] normal heptane,[30] and methyl cyclohexane,[30 31] have been identified.

2·2 Dimethyl pentane is probably also present.[31]

Straight-run Pennsylvanian gasoline has been the subject of a similar but less ambitious study by Tongberg and Fenske,[32] who have isolated therefrom by extremely efficient fractionation 2-methyl pentane, n-heptane, methylcyclohexane and n-octane. Low boiling oils from representative Japanese crude petroleums have also been examined. Mizuta[32a] has classified the gasoline fractions of these oils according to the predominant portion of their hydrocarbons, as follows: (1) High aromatic content, Shukkoho crude oil; (2) paraffinic gasoline fractions, Masuporo, Katte, Toyoiwa and Katsurani, etc.; (3) paraffinic-naphthenic gasoline, Asahikawa, Nigonikawa, etc.; and (4) naphthenic, Fureoi and Hokkaido crude oils. There appears to be some systematic connection between the hydrocarbon constituents of the gasoline fractions and the geographical distribution of the crude oils. Higher boiling fractions (over 200° C.) of Japanese crude oils have been examined by Kobayashi.[33] The identification of diolefines in the lower fractions of a vapour-phase cracked gasoline by the formation of acid anhydrides by reaction with maleic anhydride has been reported by Birch and Scott.[33a] In this way the presence of butadiene, piperylene, isoprene and cyclopentadiene was proved. The use of dehydrogenation in the presence of platinized charcoal catalyst at 300–310° C. has been advocated by Zelinskii and Kazanskii[34] as a satisfactory means of investigating the six-membered ring naphthene compounds present in the 170–200° fraction of Baku petroleum. Hitherto dehydrogenation has been considered satisfactory only in the case of fractions boiling below 150° C. because of side reactions. Using such an investigation method Zelinskii and Kazanskii have concluded that the 170–200° C. fraction of Baku petroleum consists

[28] Hicks-Bruun and Bruun, *Bur. Stand. J. Res.*, 1931, **7**, 799-809; *J. Inst. Petr. Techn.*, 1932, **18**, 69A.

[29] White and Rose, *Bur. Stand. J. Res.*, 1931, **7**, 907–911; *J. Inst. Petr. Techn.*, 1932, **18**, 70A.

[30] Hicks-Bruun and Bruun, *Bur. Stand. J. Res.*, 1932, **8**, 525–539; *J. Inst. Petr. Techn.*, 1932, **18**, 279A.

[31] Bruun and Hicks-Bruun, *Bur. Stand. J. Res.*, 1932, **9**, 53; *J. Inst. Petr. Techn.*, 1932, **18**, 404A.

[32] Tongberg and Fenske, *Ind. Eng. Chem.*, 1932, **24**, 814; *J. Inst. Petr. Techn.*, 1932, **18**, 322A.

[32a] Mizuta, *J.S.C.I.*, Japan, 1932, **35**, 157.

[33] Kobayashi, *J.S.C.I.*, Japan, 1932, **35**, 107–111.

[33a] Birch and Scott, *Ind. Eng. Chem.*, 1932, **24**, 49; *J. Inst. Petr. Techn.*, 1932, **18**, 103A.

[34] Zelenski and Kazanski, *Ber.*, 1931, **64B**, 2265–2270; *Chem. Abs.*, 1932, **26**, 77.

chiefly of cyclo-pentane derivatives, which do not undergo catalytic dehydrogenation.

The light neutral oils from lignitic tars have been examined by Titow,[35] and found to contain a mixture of aliphatic saturated and unsaturated hydrocarbons and various ketones. The latter were of aliphatic and saturated type in the low boiling fractions (up to 170° C.), and are formed by the decomposition of fatty acid salts present in the lignite. The ketones in the higher boiling fractions were cyclic in structure, and were produced during the thermal decomposition of the cyclic acids in the resinous constituents of the lignite bitumen.

The satisfactory separation of high molecular weight paraffin hydrocarbons from eicosane ($C_{20}H_{42}$) to triacontane ($C_{30}H_{62}$) by fractional distillation under a pressure of 0·001 mms. has been reported by Gilchrist and Korlik.[36] Formulæ for calculating the number of stereoisomeric and non-stereoisomeric paraffin hydrocarbons have been developed by Blair and Henze.[37]

Diisobutylene, hitherto considered to be a single hydrocarbon, has been found to consist of a mixture of two isomers :—

(*a*) 2·4·4 Trimethyl–1 pentene. BP_{760} 101·2° C. d_4^{20} 0·7151 n_D^{20} 1·4082, and

(*b*) 2·4·4 Trimethyl–2 pentene. BP_{760} 104·5° C. d_4^{20} 0·7211 n_D^{20} 1·4158,

the composition of each of which has been determined by oxidation with ozone.[38] The freezing point of iso-octane (2·2·4 Trimethyl pentane) has been determined by Bruun and Hicks-Bruun,[39] and found to be –107·41° C., as against the previous literature value of –107·8° C.

Highly purified paraffins from $C_{26}H_{54}$ to $C_{36}H_{74}$ and long chain ketones and secondary alcohols have been synthesised, and their crystal spacings determined,[40] and the viscosities of gaseous n-heptane, n-octane and n-nonane have been measured.[41] From the latter determinations Sutherland constants and the collision

[35] Titow, *Brenn.-Chem.*, 1932, **13**, 306–308 ; *J. Inst. Petr. Techn.*, 1932, **18**, 412A.

[36] Gilchrist and Korlik, *J.C.S.*, 1932, **135**, 1992 ; *J. Inst. Petr. Techn.*, 1932, **18**, 404A.

[37] Blair and Henze, *J.A.C.S.*, 1932, **54**, 1538 ; *J. Inst. Petr. Techn.*, 1932, **18**, 226A.

[38] Tongberg, Pickens, Fenske and Whitmore, *J.A.C.S.*, 1932, **54**, 3706–3710 : *J. Inst. Petr. Techn.*, 1932, **18**, 404A.

[39] Bruun and Hicks-Bruun, *Bur. Stand. J. Res.*, 1932, **9**, 269 ; *J. Inst. Petr. Techn.*, 1932, **18**, 405A.

[40] Piper, Chibnell, Hopkins, Pollard, Smith and Williams, *Bio. Chem. J.*, 1931, **25**, 2072.

[41] Melaven and Mack, *J.A.S.C.*, 1932, **54**, 888 ; *J. Inst. Petr. Techn.*, 1932, **18**, 185A.

areas of the molecules have been calculated, and it has been shown to be very probable that these carbon chain molecules do not exist in the extended form in the gas phase, but are coiled up, on the average, into the shape of a loose helix.[41] Parks and Huffman[42] have determined the heats of fusion of 59 hydrocarbons, including normal and branched chain paraffins, aliphatic olefines and aromatics and naphthenes, using the Nernst method with an aneroid calorimeter.

The application of infra red absorption spectra to the study of hydrocarbons and oils has been examined by Lambert and Lecomte,[43] and the reactions of hydrocarbons in the glow discharge have been studied by Linder and Davis.[44]

A number of hydrocarbons have been bombarded with cathode rays, and the volume and composition of the gaseous products determined.[45] Saturated hydrocarbons give large, and unsaturated hydrocarbons give small, amounts of gas consisting of hydrogen and saturated hydrocarbons, while aromatic hydrocarbons give practically no gaseous products; branched chain hydrocarbons give more methane and other gaseous hydrocarbons than straight chain compounds. The reaction is shown to be analogous to that of hydrocarbons under the influence of the corona discharge or α particles.

Experiments on the decomposition of tetra ethyl lead indicating that free ethyl radicles are formed have been described. In these experiments tetra ethyl lead was decomposed, and the resulting free ethyl radicles allowed to react with mirrors of lead, arsenic, antimony, zinc and cadmium.[46] The action of benzol peroxide on triethylmethane has been reported upon,[47] and the detection and separation of tertiary hydrocarbons from hydrocarbon mixtures by means of antimony pentachloride has been described.[48]

Vlugter, Waterman and Van Wasten[49] have made a valuable contribution on the subject of hydrocarbon examination and analysis, and have developed improved methods involving measurements of specific refraction, aniline point and molecular weight.

[42] Parks and Huffman, *Ind. Eng. Chem.*, 1931, **23**, 1138–1139; *J. Inst. Petr. Techn.*, 1932, **18**, 29A.

[43] Lambert and Lecomte, *Ann. des Comb. Liq.*, 1931, **6**, 1001–1083; *J. Inst. Petr. Techn.*, 1932, **18**, 227A.

[44] Linder and Davis, *J. Phys. Chem.*, 1931, **35**, 3649; *J. Inst. Petr. Techn.*, 1932, **18**, 67A.

[45] Schoepfle and Fellows, *Ind. Eng. Chem.*, 1931, **23**, 1396–1398; *J. Inst. Petr. Techn.*, 1932, **18**, 68A.

[46] Pareth and Lautsch, *Ber.*, 1931, **64B**, 2702–2707; *Chem. Abs.*, 1932, **26**, 1232.

[47] Boesken and Wildschut, *Rec. trav. Chim.*, 1932, **51**, 168–173.

[48] Schaarschmidt, *Petr. Z.*, 1932, **28** (12), 1–4.

[49] Vlugter, Waterman and Van Westen, *J. Inst. Petr. Techn.*, 1932, **18**, 735.

The Chemistry of Polymerisation continues to attract attention. Conant and Peterson have studied polymerisation reactions under pressure, and have attempted to determine the mechanism of polymerisation reactions. Their previous work has shown that peroxides and ozonides are effective polymerisation catalysts, but that catalysts are not essential since a sample of isoprene distilled in nitrogen and compressed without exposure to air polymerises at a rate only slightly less than that of material freshly distilled in air. They have recently[50] revised their conclusions, and consider that peroxide catalysis is essential to polymerisation, and that the effect of increased pressure is only to accelerate the reaction. It is suggested that the mechanism of polymerisation is a series of chain reactions initiated in the liquid by the spontaneous decomposition of the peroxide from time to time. The accelerating effect of high pressures is due to the orientation of the molecule of isoprene or aldehyde into a more compact shape in which longer reaction chains would be propagated by the spontaneous decomposition of a single peroxide molecule. Cyclohexene-oxide has been polymerised with great difficulty. The rates of polymerisation of diisopropenyl, myrcene, divinyl hydrocarbons and allene hydrocarbons have been studied by Gapon,[51] and velocity constants, temperature coefficients, heats of activation and reaction constants determined.

Thomas and Carmody[52] have found that no apparent chemical action takes place on mixing isoprene with aluminium chloride, but on prolonged standing a polymer, insoluble in hydrocarbon solvents, is produced. If, however, pentene–2 is added to the isoprene-aluminium chloride mixture, a reaction commences immediately and results in the formation of two polymers, one soluble and the other insoluble in hydrocarbon solvent. The amount of soluble polymer formed was found to be a function of the amount of pentene–2 present, while its hardness and also the yield of insoluble polymer were found to be inverse functions of the amount of pentene–2 present.

The influence of methyl and phenyl substitution on the polymerisability of butadiene has been studied by Whitby and Gollay[53] in an extension of their previous work on the polymerisation of butadiene. Results obtained with dimethyl butadienes show

[50] Conant and Peterson, *J.A.C.S.*, 1932, **54**, 628; *J. Inst. Petr. Techn.*, 1932, **18**, 104A.
[51] Capon, *J. Gen. Chem.* (U.S.S.R.), 1931, **1**, 496, 502, 765, 770; *Chem. Abs.*, 1932, **26**, 4580.
[52] Thomas and Carmody, *J.A.C.S.*, 1932, **54**, 2480; *J. Inst. Petr. Techn.*, 1932, **18**, 321A.
[53] Whitby and Gollay, *Canad. J. Res.*, 1932, **6**, 280–291; *J. Inst. Petr. Techn.*, 1932, **18**, 359A.

that an increase in the number of substituent groups of a given kind reduces the ease of polymerisation, especially to high molecular polymers. Results obtained with the trimethyl and tetramethyl butadienes indicate that terminal substitution retards polymerisation.

Niewland, Calcott, Downing and Carter[54] have obtained monovinyl acetylene, divinyl acetylene and a tetrameride–1·5·7 octatriene–3 ine by the controlled polymerisation of acetylene. Divinylacetylene has been found to be extremely dangerous to handle, and can only be distilled with considerable risk of explosion. It readily polymerises to form a gel, and finally a hard resin. The reversible polymerisation of six-membered cyclic esters has been studied by Carathers, Dorough and Van Datta.[55] Egloff, Lowry and Schaad[56] have contributed an excellent review on the polymerisation and decomposition of acetylene hydrocarbons.

The Chemistry of Cracking and Pyrolysis.

The thermal reactions of cycloparaffins and cyclo-olefines have been reviewed by Egloff, Bollman and Levinson,[57] who have classified the reactions taking place as follows: (1) carbon-hydrogen scission; (2) hydrogenation or dehydrogenation; (3) polymerisation and depolymerisation, and (4) isomerisation. Any one of these reactions may take place when a hydrocarbon is heated, and the stability of the ring structure and the relation of the ring to the whole molecule are criteria by which the pyrolysis may be postulated. With regard to polymethylene rings, cyclopropane, cyclobutane, cyclooctane and cycloheptane undergo a breaking of the carbon hydrogen bond, the ease of rupture decreasing in the order given. Cyclohexane gives a carbon-hydrogen scission more readily than a carbon-carbon scission, while cyclopentane is resistant to either type of scission. These decompositions are evidenced by the fact that in the first polymethylenes mentioned above, ring rupture and isomerisation occur to form more stable compounds. Cyclopropane yields propylene and cycloheptane gives methylcyclohexane, although some dehydrogenation also occurs to form bicycloheptane.

The mechanism of the formation of aromatics from lower

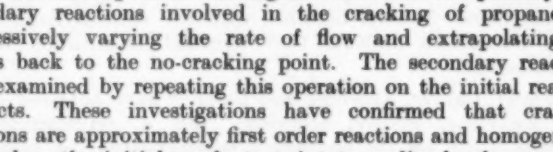
[54] Niewland, Calcott, Downing and Carter, *J.A.C.S.*, 1931, **53**, 4197; *J. Inst. Petr. Techn.*, 1932, **18**, 30A.

[55] Carathers, Dorough and Van Datta, *J.A.C.S.*, 1932, **54**, 761; *J. Inst. Petr. Techn.*, 1932, **18**, 104A.

[56] Egloff, Lowry and Schaad, *J. Phys. Chem.*, 1932, **36**, 1457–1520; *J. Inst. Petr. Techn.*, 1932, **18**, 278A.

[57] Egloff, Bollman and Levinson, *J. Phys. Chem.*, 1931, **35**, 3489; *J. Inst. Petr. Techn.*, 1932, **18**, 67A.

paraffins by pyrolysis has been examined by Schneider and Frolich,[58] who have attempted to distinguish between the primary and secondary reactions involved in the cracking of propane, by progressively varying the rate of flow and extrapolating the results back to the no-cracking point. The secondary reactions were examined by repeating this operation on the initial reaction products. These investigations have confirmed that cracking reactions are approximately first order reactions and homogeneous even when the initial products point to a dimolecular reaction. They suggest the following cracking mechanism :—



With regard to the pyrolysis of methane, a preliminary report on experiments conducted at the United States Bureau of Mines has recently appeared.[59] The following results have been obtained :—

(1) Pyrolysis of methane yields higher hydrocarbons, among which the following have been identified : ethylene, acetylene, benzene, naphthalene, anthracene and pyrene.
(2) Yields at atmospheric pressure depend upon temperature and rate of flow through the cracking zone.
(3) Ethylene predominates at the commencement of the reaction, other hydrocarbons being formed subsequently, but it is not yet known whether the light oil formed proceeds from ethylene or acetylene.
(4) Dilution with either nitrogen or hydrogen affects the yields of products obtained and increases the proportion of both ethylene and acetylene.
(5) Admixture of ethane increases the yields of all products.
(6) Relationships between yield and the variables, temperature and space velocity, have been found to exist.

Further work at the Bureau of Mines is in progress.

The pyrolysis of gases other than methane has been studied by Frey and Hepp,[60] particularly with regard to the time factor, and it has been shown that pyrolysis proceeds through a rapid endo-

[58] Schneider and Frolich, *Ind. Eng. Chem.*, 1931, **23**, 1405–1410 ; *J. Inst. Petr. Techn.*, 1932, **18**, 68A.
[59] Smith, Grandone and Rall, *U.S. Bur. Min. Repts. Invest.*, 3143, October, 1931 ; *Oil & Gas J.*, 1931, **30** (24), 90 ; *J. Inst. Petr. Techn.*, 1932, **18**, 28A.
[60] Frey and Hepp, *Ind. Eng. Chem.*, 1932, **24**, 282 ; *J. Inst. Petr. Techn.*, 1932, **18**, 139A.

thermic decomposition in which simple olefines are formed. This reaction is followed by one of a much slower endothermic nature, during which the olefines are converted into aromatics. In the neighbourhood of 850° C. butadiene and cyclopentadiene were found to be the chief low boiling products, apart from benzene and toluene which predominate in the volatile oils.

According to Neuhaus and Marek[61] the pyrolysis of butane at 600° C. and 650° C. yields the following primary products in the order of their relative importance : methane and propylene, ethane and ethylene, hydrogen, butylene and propane. No butadiene, aromatic hydrocarbon or any hydrocarbon of a higher molecular weight than butane was detected in the reaction products at these temperatures. The production of butenes by the pyrolysis of normal chlorobutanes has been described by Weston and Hass.[62] At 550° C. the pyrolysis of 1-chlorobutane and at 500° C. the pyrolysis of 2-chlorobutane, are homogeneous vapour-phase reactions, the former giving all 1-butene and the latter yielding a mixture consisting of one-third 1-butene and two-thirds 2-butene, namely cis 2-butene and trans 2-butene. It is not definitely known whether the butenes are re-arranged in contact with the catalyst (calcium chloride) or whether the catalyst causes the reaction to proceed in such a way as to product the 2-butenes directly from the chlorobutanes.

Synthetic high boiling paraffinic and olefinic hydrocarbons have been submitted to cracking at 425° C. and for various reaction times by Tilichev and Feigin.[63] Hugel[64] has presented a general review on the cracking of pure hydrocarbons.

Payne and Lowry[65] have made a study of the composition of a highly cracked gasoline, and the changes in composition effected on subjecting this material to heat treatment at temperatures of about 300° C. Such heat treatment decreased the unsaturated hydrocarbon content of the gasoline and increased the naphthenic hydrocarbon content, while polymerisation was considered responsible for the following changes : (*a*) increase of material boiling above 201·5° C. from 15·79 to 20·54 per cent ; (*b*) disappearance of the probable presence of cyclo-olefines ; and (*c*) the forma-

[61] Neuhaus and Marek, *Ind. Eng. Chem.*, 1932, **24**, 400 ; *J. Inst. Petr. Techn.*, 1932, **18**, 187A.

[62] Weston and Hass, *J.A.C.S.*, 1932, **54**, 3337–3343 ; *J. Inst. Petr. Techn.*, 1932, **18**, 387A.

[63] Tilicheev and Feigin, *Repts. Conf. Cracking Hydrogenation, Grozny*, 1931, **1**, 267–297 ; *Chem. Abs.*, 1932, **26**, 1105.

[64] Hugel, *Trans. 2nd Wld. Power Conf.*, 1930, **8**, 56–71 ; *Chem. Abs.*, 1932, **26**, 2853.

[65] Payne and Lowry, *Ind. Eng. Chem.*, 1932, **24**, 432 ; *J. Inst. Petr. Techn.*, 1932, **18**, 163A.

tion of hydrocarbons containing hydrogen atoms easily replaceable by halogen.

Experiments on the cracking of fish oils have been reported by Faragher, Egloff and Morrell.[66]

Sulphur Compounds.

A number of normal and α-secondary mercaptans from methyl mercaptan to nonyl mercaptan have been prepared and their physical properties recorded by Ellis and Reid.[67] Various anthraquinone α-alkyl thio ethers have been synthesised from the high boiling normal mercaptans. 2·4 Dinitrochlorobenzene has been proposed as a new reagent for the identification of mercaptans by Bost, Turner and Norton.[68] This reagent is inexpensive and forms solid sulphides which can be rapidly oxidised to the corresponding sulphones.

The action of mercaptans in hydrocarbon solution on copper and copper sulphide, to form cuprous mercaptides and disulphides has been reported.[69] The insoluble cuprous derivatives of the primary and secondary mercaptans remain on the surface of the copper, while those of the higher secondary mercaptans pass into solution, colouring the hydrocarbons. Alkyl sulphides and disulphides have no action upon copper or copper sulphide. According to Duncan and Ott,[70] when benzene solutions of sulphur and sec-butyl lead mercaptide are shaken together in varying proportions of S/Pb=8 or higher, practically pure lead disulphide is formed, of a deep reddish brown colour, insoluble in water and common organic solvents. The lead disulphide is unstable and readily decomposes into lead sulphide and sulphur. No higher polysulphides were obtained in this reaction.

The analytical reactions of alkyl mercaptans and alkyl sulphides in benzene solution have been considered by Sampey and Reid,[71] and by Sampey, Slagle and Reid[72] respectively.

The production of hydrogen sulphide by heating paraffin and other hydrocarbon mixtures with sulphur has been dealt with by

[66] Faragher, Egloff and Morrell, *Ind. Eng. Chem.*, 1932, **24**, 440; *J. Inst. Petr. Techn.*, 1932, **18**, 181A.
[67] Ellis and Reid, *J.A.C.S.*, 1932, **54**, 1674–1687; *J. Inst. Petr. Techn.*, 1932, **18**, 226A.
[68] Bost, Turner and Norton, *J.A.C.S.*, 1932, **54**, 1985-1987; *J. Inst. Petr. Techn.*, 1932, **18**, 280A.
[69] Slagle and Reid, *Ind. Eng. Chem.*, 1932, **24**, 448–451; *J. Inst. Petr. Techn.*, 1932, **18**, 228A.
[70] Duncan and Ott, *J.A.C.S.*, 1931, **53**, 3940–3949; *J. Inst. Petr. Techn.*, 1932, **18**, 30A.
[71] Sampey and Reid, *J.A.C.S.*, 1932, **54**, 3404–3409; *J. Inst. Petr. Techn.*, 1932, **18**, 403A.
[72] Sampey, Slagle and Reid, *J.A.C.S.*, 1932, **54**, 3401-3404; *J. Inst. Petr. Techn.*, 1932, **18**, 403A.

Scudder and Lyons,[73] and the effect of various catalysts studied. Lamp black and aluminium chloride were found to have pronounced catalytic effect. Lèclere and Lèclere[74] have sulphonated the therapeutically valuable distillates from bituminous shales and saponified the resulting thiophenic sulphonic acids with boiling water. They thus obtained a yield of 8 per cent. of lower thiophene hydrocarbons, principally α N.propyl thiophenes, b.p. 157·5° C., α isopropyl thiophene b.p. 153·4° C. and β isopropyl thiophene, b.p. 157·8° C. According to Ruhemann and Baumbach,[75] the thiophenic sulphur compounds present in brown coal benzenes are not sulphonated by concentrated sulphuric acid, but condense with cyclic unsaturated hydrocarbons of the terpene series to form dimolecular compounds analagous to the $\alpha\beta$ propane derivatives formed by the condensation of xylene with styrene. Thus the 140–150° C. fraction of a mid-German low-temperature tar treated with concentrated sulphuric acid gave a compound $C_{15}H_{22}S$, which, thermally depolymerised, yielded 2·3 dimethyl thiophene and a hydroaromatic hydrocarbon (C_9H_{14}) of the terpene series.

Oxidation of Petroleum Hydrocarbons.

This is a subject of ever growing importance owing to its intimate connection with such phenomena as the knocking of gasolines and Diesel oils, gum formation in gasolines, sludge formation in transformer and lubricating oils, etc., as well as in the manufacture of valuable oxygenated chemical materials from petroleums.

A valuable review on auto-oxidation has been contributed by Milas,[76] in which special reference is given to the electronic theory. This postulates a preliminary addition of oxygen atoms containing molecular valence electrons, with the subsequent formation of highly metastable peroxides having a high energy content. These peroxides may transfer their excess energy to other molecules, and thereby initiate new reaction chains either by reverting to ordinary peroxides or by causing intermolecular re-arrangements with subsequent splitting of hydrogen peroxide or other organic peroxides. Auto-oxidation reactions may be recognised by the facts that: (1) they are auto-catalytic; (2) they are susceptible to positive or negative catalysts; (3) they induce the oxidation of other substances relatively unaffected by free oxygen; (4) they induce the polymerisation of various auto-oxidants; (5) in certain cases auto-oxidation reactions are chemi-luminescent; and (6)

[73] Scudder and Lyons, *Proc. Indiana Acad. Sci.*, 1931, **40**, 185–188; *Chem. Abs.*, 1932, **26**, 1234.
[74] Lèclere and Lèclere, *Compt. rend.*, 1932, **194**, 286–287.
[75] Ruhemann and Baumbach, *Braunkohle*, 1932, **31**, 549, 565.
[76] Milas, *Chem. Revs.*, 1932, **10**, 295-364; *J. Inst. Petr. Techn.*, 1932, **18**, 320A.

susceptibility to auto-oxidation is frequently governed by the structure of the auto-oxidant. The oxidation reactions of saturated and unsaturated hydrocarbons are of the non-reversible type, and it has been shown that several saturated hydrocarbons follow a chain mechanism. Chain propagation is assumed to take place when the intermediate oxygenated products collide with fresh molecules of the hydrocarbon and collision with oxygen molecules results in the destruction of the reaction chain.

King and Edgcombe[77] have studied the rates of oxidation of hydrogen, carbon monoxide and paraffin hydrocarbons by copper oxide at elevated temperatures (280° C.), and found that the relative rates of oxidation of methane, ethane, propane and butane at this temperature, expressed as volume per cent., after 10 min. contact, were nil, 0·8, 1·0 and 1·4 respectively.

The slow combustion of methane at high pressures has been considered by Newitt and Haffner,[78] who form the following conclusions. Considerable quantities of the primary product, methanol, survive and can be isolated. As combustion proceeds in an 8 : 1 methane oxygen mixture the rate of formation of methanol increases with the methane-oxygen ratio until a point is reached when the concentration of steam and carbon dioxide in the products begin to exert a retarding effect. The effect of increasing pressure is not only to increase the amounts of methanol and formaldehyde surviving, but also to increase the ratio methanol/formaldehyde. The oxidation of methane under the conditions employed by Newitt and Haffner is mainly a surface effect, and is characterised by a marked induction period. Further work on the slow combustion of methane has been carried out by Bone and Allum[79] which demonstrates a case of direct hydrocarbon oxidation "entirely uncomplicated by any sign of peroxidation." The results are held by Bone and Allum to fulfil the predictions of Bone's hydroxylation theory. The oxidation of pentane and other hydrocarbons has been carried out by Pidgeon and Egerton.[80] In the oxidation of pentane by oxygen, the temperature at which reaction proceeds rapidly increases as the pressure decreases and is lowest for a 50/50 C_5H_{12}—O_2 mixture. The oxidation has the general characteristics of a chain reaction. In the slow combustion of hexane amylene valeraldehyde and isoamyl alcohol, the temperature at which oxidation becomes rapid and the influence of total pressure and concentration on the reaction have been

[77] King and Edgecombe, *Fuel Res. Techn.*, Paper 32, 1931.
[78] Newitt and Haffner, *Proc. Roy. Soc.*, 1932, **A134**, 591-604.
[79] Bone and Allum, *Proc. Roy. Soc.*, 1932, **A134**, 578–591.
[80] Pidgeon and Egerton, *J.C.S.*, 1932, **135**, 661-676; *J. Inst. Petr. Techn.*, 1932, **18**, 138A.

noted. The decrease in pressure in the case of hexane is mainly due to the formation of a condensible product, but with amylene to direct absorption of oxygen. Active hexane has been found to initiate reaction in pentane mixtures, while valeraldehyde is still more effective and amylene and iso amyl alcohol are ineffective. Pidgeon and Egerton point out that these facts do not accord well either with primary dehydrogenation of the reacting molecule or with hydroxylation.

Green has studied the catalytic partial oxidation of toluene,[81] and of naphthalene and tetrahydronaphthalene.[82] At temperatures not above 450° C., using a vanadium oxide catalyst, a combined yield of benzoic acid, benzaldehyde and anthraquinone of over 60 per cent. was obtained; but at temperatures above 450° C. the proportion of toluene converted to carbon dioxide and water increased markedly. Similar results were obtained using molybdenum oxide catalyst. Naphthalene gave a 66 per cent. yield of phthalic anhydride at 370° C. with a vanadium pentoxide catalyst.

The vapour-phase catalytic oxidation of various hydrocarbons has also been carried out by Wilken-Jorden.[83] With manganese vanadate catalyst, p-benzoquinone was found to be an intermediate oxidation product of benzene, the oxidation becoming measurable at 450° C. and increasing with increasing temperature. Carbon monoxide appeared with carbon dioxide in the earliest stages of the oxidation. With toluene, the oxidation products obtained at higher temperatures contained benzaldehyde and p.p′ ditolyl. Other hydrocarbons examined included xylene, cyclohexane, cyclohexene, heptane, cyclopentadiene and methyl ethylene.

Riley and Friend[84] have found selenium dioxide to be an effective oxidising agent for some unsaturated hydrocarbons, its reaction with ethylene being :—

$$3\ SeO_2 + 2\ C_2H_4 = 2\ (CHO)_2 + 3\ Se + 2\ H_2O.$$

The reaction between oxygen and propylene at temperatures of 500–600° C. has been studied by Lenher.[85] Oxidation and pyrolysis have been found to take place, and the oxidation products were acetaldehyde, formaldehyde, formic acid, oxides of carbon

[81] Green, *J.S.C.I.*, 1932, **51**, 123T.–126T.; *J. Inst. Petr. Techn.*, 1932, **18**, 186A.

[82] Green, *J.S.C.I.*, 1932, **51**, 159T–160T; *J. Inst. Petr. Techn.*, 1932, **18**, 281A.

[83] Wilken and Jorden, *J. Chem. Met. Min. Soc. S.A.*, 1932, **32**, 283–295; *Chem. Abs.*, 1932, **26**, 5406.

[84] Riley and Friend, *J.C.S.*, 1932, **135**, 2342–2344.

[85] Lenher, *J.A.C.S.*, 1932, **54**, 1830–1837; *J. Inst. Petr. Techn.*, 1932, **18**, 278A.

and water. The primary products of the pyrolysis (up to 530° C.) were higher mono-olefines, butylenes, amylenes and hexylenes; secondary products were olefines, paraffins and hydrogen. Chatterjee[86] has obtained about 20 per cent. of higher aldehydes by passing paraffin vapour mixed with air over a reduced nickel catalyst. As indicating the striking catalytic activity of copper in hydrocarbon oxidations certain ageing tests on lubricating oils in copper vessels by Damien[87] are of interest.

The oxidation of higher hydrocarbons and their mixtures has been studied by Ivanov,[88] who found that paraffin base oils yield more fatty and less hydroxy acids than naphthene base oils when exposed to identical oxidation conditions. In the oxidation of high boiling oils in the presence of sodium, lithium, manganese, iron, lead and copper naphthenates a 30 per cent. conversion into high molecular weight acids was obtained at 15 atmospheres oxygen pressure. Similar investigations have been reported by Tuichinin and Ivanov,[89] while according to Yamada[90] the oxidation of refined mineral oil is accelerated by the addition of organic acids. The effect of various catalysts on the oxidation of paraffin oil by means of bubbling oxygen at 130° C. has also been studied.[91] Copper, nickel, nickel oxide, anthraquinone and copper oxide were found to be positive catalysts, while aniline, hexadecane, iron oxide, phenol and water acted as oxidation inhibitors.

The relationship between gasoline knock ratings and oxidation characteristics has been considered by Mondain-Monval,[92] who has given evidence on the possibility of peroxide formation in the cylinders of operating engines. The conclusions arrived at are as follows: under the ordinary running conditions peroxides cannot form in the engine cylinder, because the temperature of the gasoline-air mixture is never high enough, but if the compression is increased the temperature reached by the gas mixture at the end of compression rises considerably and peroxides are then formed in appreciable amounts, the velocity of their formation being quite high. The same phenomena occur when the engine heats up abnormally—*e.g.*, through defective cooling. It is considered probable that the presence of peroxides in sufficient

[86] Chatterjee, *J. Indian Chem. Soc.*, 1931, **8**, 533.
[87] Damien, *Chim. et Ind.*, Spec. No., March, 1932, 5; *Chem. Abs.*, 1932, **26**, 3657.
[88] Ivanov. *Neft. Khoz.*, 1932, **22**, 85–94; *Chem. Abs.*, 1932, **26**, 4455.
[89] Tuichinin and Ivanov, *Masloboino Zhirovol Delo*, 1930, **3**, 36–43, 4-5, 40–47; *Chem. Abs.*, 1932, **26**, 4165.
[90] Yamada, *J.S.C.I.*, Japan, 1932, **35**, Suppl. binding, 202; *Chem. Abs.*, 1932, **26**, 4703.
[91] Arditti, *Compt. rend.*, 1932, **195**, 136–137.
[92] Mondain-Monval, *Bull. Soc. Encour. Ind. Natl.*, 1932, **131**, 360–365.

quantities in the compressed gas mixture considerably increases the rate of combustion ; each molecule of peroxide can be considered as a centre containing a large amount of latent energy, causing almost spontaneous combustion of the surrounding gas and producing an enormously rapid propagation of the flame. It follows that the degree of knocking is intimately related to the amount of peroxides formed in the gas mixture. These conclusions support the theory of Dumanois.[93]

Graefe[94] has reported the formation of nitro bodies in internal-combustion engines, and maintains that such bodies are produced by the combination of atmospheric nitrogen and oxygen in the engine ; the high initial pressure in Diesel engines is also said to favour the formation of nitro bodies by the decomposition of lubricating oils.

Asphalts and Pitches.

The chemical composition of asphalts and asphaltic material has been considered by Kalichevsky and Fulton,[95] who have also presented a general review of preceding work. These investigators have evolved a scheme of analysis for the five groups of compounds found in asphalts—namely, asphaltic acids, asphaltic anhydrides, asphaltenes, asphaltic resins and residual oil, based upon petroleum ether extraction. Not much is known about asphaltic acids and anhydrides, they have a relatively high specific gravity, are sparingly soluble in light naphtha and are not very stable. Asphaltenes are dark brown to black in colour, have no apparent melting point when purified, decompose to gas and coke at 300° C., and are insoluble in petroleum ether, alcohol, water and similar solvents, but soluble in aromatic hydrocarbons and carbon disulphide, etc. They are colloids with an extremely high degree of dispersion.

Asphaltenes are considered to be lyophilic with respect to aromatic hydrocarbons and allied solvents in which they are highly dispersed and soluble, while their apparent solubility in kerosine is due to the presence of occluded resins which act as protective colloids. Rubber may act as a protective colloid for the preparation of a stable suspension of asphaltenes in gasoline. The chemical composition of asphaltenes is not well known, but it is believed that though oxygen and sulphur may be present they are not essential constituents, for an asphaltene of the empirical formula $C_{90}H_{160}$ and sp. gr. 1·0230 has been isolated. The oxygen

[93] Dumanois, *Chem. Abs.*, 1928, **22**, 1466.
[94] Graefe, *Petr. Z.*, 8.6.32, **28** (23), *Motorenbetrien*, **5** (6), 5–6 ; *J. Inst. Petr. Techn.*, 1932, **18**, 384A.
[95] Kalichevsky and Fulton, *Nat. Petr. News*, 1931, **23** (51), 33–36 ; *J. Inst. Petr. Techn.*, 1932, **18**, 55A.

content of a blown residuum does not necessarily change, but oxygen, usually in the form of water, is found in the volatile reaction product, and the asphaltenes so formed are not different in properties from the naturally occurring bodies. Asphaltenes from acid sludge are different in structure, and it is suggested that they are oxonium compounds of the form :—

$$\begin{array}{ccccc} R' & - & O & - & R'' \\ H & & HSO_2 & & OH. \end{array}$$

They are soluble in basic solvents and can be coagulated by heating to 100° C. Asphaltenes are believed to be formed from the aromatic constituents of an oil by condensation and polymerisation, asphaltic resins being an intermediate stage. Naphthenes and paraffins, if first heated with sulphur and then oxidised with air, have yielded asphaltenes of the composition C 71·62 per cent., H 6·28 per cent., O 13·48 per cent., S 8·08 per cent. Asphaltic resins are considered to consist essentially of polycyclic compounds similar to the terpenes, and they form true solutions in petroleum hydrocarbons. In general their molecular weights are higher than those of the oil fractions in which they occur.

The subject of asphalts has also been dealt with in a review by Baskin,[96] who points out that the various constituents of asphalts have very different properties in asphalts of different origins, and that the mutual solubility of these constituents play an important part in determining the stability of the asphalts.

The structure of pitch obtained by the dry distillation of Saare coal has been investigated by Hugel and Frangopol[97] by hydrogenation at 350–400° C. under a pressure of 130 kgs./cm² with sodium hydride catalyst. This treatment resulted in the formation of comparatively few aromatic polycyclic hydrocarbons such as anthracene, dimethyl anthracene, pyrene, etc., etc. Relatively small amounts of liquid aromatic polycyclic hydrocarbons were also found.

It was concluded that such pitches consist essentially of aromatic polycyclic hydrocarbons. Tetramethyl picene approximates more nearly to the bituminous pitch oil in its properties.

---

[96] Baskin, *Oil & Gas J.*, 14.7.32, **31** (8), 36 ; *J. Inst. Petr. Techn.*, 1932, **18**, 349A.

[97] Hugel and Frangopol, *Ann. des Comb. Liq.*, 1932, **7**, 225–238, 417–467 *J. Inst. Petr. Techn.*, 1932, **18**, 467A.

Statistics.

By GEORGE SELL (Member).

World's Production.—Since the year 1929, when the world's production of crude petroleum reached the record of over 206 million metric tons, the annual production has continued to decrease. The figures for 1932 which are so far available indicate that the production for that year showed a decrease of about 11,260,000 metric tons, or 6 per cent., as compared with 1931. Table I. gives the world's production by countries for the years

TABLE I.

World's Production of Crude Petroleum.

In thousands of metric tons.

Country.	1930.	Per-centage of Total.	1931.	Per-centage of Total.	1932.	Per-centage of Total.
United States ..	123,117	63·1	116,586	61·3	107,102	59·9
U.S.S.R.	17,221	8·8	22,629	11·9	19,668	11·0
Venezuela	20,252	10·4	17,543	9·2	17,493	9·8
Rumania	5,744	2·8	6,658	3·5	7,337	4·1
Persia	6,034	3·1	5,843	3·1	6,604	3·7
Dutch East Indies ..	5,531	2·8	4,713	2·5	5,028	2·8
Mexico	5,914	3·0	4,935	2·6	4,850	2·7
Colombia	2,905	1·5	2,605	1·4	2,345	1·3
Argentina	1,301	0·7	1,697	0·9	1,884	1·0
Trinidad	1,315	0·7	1,361	0·7	1,411	0·8
Peru	1,656	0·9	1,345	0·7	1,320	0·7
India	1,185	0·6	1,162	0·6	1,124	0·6
Poland	663		631		557	
Sakhalin	267		401		415	
Sarawak	707		552		400	
Egypt	285		291		256	
Japan	271		273		217	
Germany	173		227		230	
Ecuador	221	1·6	252	1·6	228	1·6
Canada	186		188		128	
Iraq	122		111		122	
France	76		74		76	
Czecho-Slovakia ..	23		20		28	
Italy	8		16		28	
Bolivia	7		3		5	
Other countires ..	8		8		8	
Total	195,192	100·0	190,124	100·0	178,864	100·0

1930 to 1932, the figures for the latter year being subject to slight correction when the final estimates are available. From this table it is seen that the decrease has been more or less general all over the world, and that there are practically no changes in the positions of the various countries as regards their percentage production.

While some of the decreases in production may be attributed to natural decline, it is also probable that the excess of supply over demand, and the consequent low prices obtaining at present for petroleum products, is to some extent a contributing factor in that very little search for new sources of supply is being undertaken. The various curtailment schemes which have been put into force in different countries are also reflected in the production figures, and the consequences are particularly evident in the United States. For the first time since 1906 the production in the United States has fallen below the level of 60 per cent. of the world's total.

Details of the production in the United States by fields are given in Table II., and it will be seen that in 1932 the production decreased by about 8 per cent. from the 1931 total. Compared with the peak year, 1929, when the production was over 138 million metric tons, the 1932 figure is about 23 per cent. less.

TABLE II.

Production of Crude Petroleum in the United States.
In thousands of metric tons.

Field.	1930.	1931.	1932.
Appalachian	4,676	4,165	4,053
Lima, N.E. Indiana and Michigan	723	677	1,072
Illinois and S.E. Indiana ..	916	800	745
Mid-Continent	72,862	74,484	67,167
Gulf Coast	9,552	7,889	7,280
Rocky Mountain	3,221	2,704	2,384
California	31,167	25,867	24,401
	123,117	116,586	107,102

Motor Fuel.—The production of motor fuel in the United States in 1932, as reported by the U.S. Bureau of Mines, decreased by about 9 per cent., as compared with 1931. The figures are given in Table III.

TABLE III.

Production of Motor Fuel in the United States.
In thousands of barrels.

	1931.	Percentage of Total.	1932.	Percentage of Total.
Straight-run gasoline ..	219,957	50·3	195,386	49·0
Cracked gasoline ..	176,437	40·3	170,905	42·8
Natural gasoline ..	39,515	9·0	31,710	7·9
Benzole	1,826	0·4	1,144	0·3
	437,735	100·0	399,145	100·0

TABLE IV.

World Consumption of Motor Fuels.

(*Millions of barrels of 42 U.S. gallons/year.*)

	Gasoline.	Kerosine.*	Gas and Diesel Oil.	Alcohol.	Benzole.	Blended Fuels.	Known Total.
United Kingdom	30·9	7·6	4·2	negligible	0·9	2·0	45·6
France	19·4	1·7	2·2	0·2	0·4	—	23·9
Canada	18·0	1·3	—	—	—	—	19·3
Germany	14·7	1·6	—	0·4	2·3	—	19·0
Australia	6·4	0·7	0·8	negligible	negligible	0·1	8·0
Argentina	5·8	0·5	0·8	,,	—	—	7·1
Italy	4·0	1·4	negligible	,,	—	negligible	5·4
Japan	3·5	0·8	1·4	—	negligible	0·1	5·8
Spain	3·4	negligible	0·5	—	,,	—	3·9
Sweden	2·8	0·6	negligible	negligible	—	0·2	3·6
India	2·4	7·5	,,	—	negligible	—	9·9
Belgium	2·3	0·7	,,	—	0·1	(*a*)	3·1
Mexico	2·1	negligible	,,	—	negligible	negligible	2·1
Denmark	2·0	0·8	,,	—	,,	,,	2·8
Brazil	1·8	0·8	,,	negligible	—	,,	2·6
Union of South Africa	1·8	0·4	,,	,,	—	,,	2·2
New Zealand	1·8	negligible	,,	—	negligible	,,	1·8
Dutch Indies	1·6	2·3	1·8	—	—	—	5·7
Czecho-Slovakia	1·6	0·1	0·2	negligible	0·1	negligible	2·0
Switzerland	1·3	negligible	negligible	—	negligible	,,	1·3
Austria	1·2	0·3	0·3	—	,,	0·1	1·9
Other countries	11·5	5·9	4·1	0·2	0·2	0·3	22·2
Total	140·3	35·0	16·3	0·8	4·0	2·8	199·2
United States	401·6	31·3	over 25	—	1·8	—	459·7

* Generally includes all uses, probably mainly as an illuminant.

(*a*) Most " gasolines " contain 6 per cent. benzole.

Figures for the total annual world consumption of various motor fuels have been published by the U.S. Department of Commerce,[1] and a summary is given in Table IV.

United Kingdom Imports.—According to the Board of Trade Returns, as given in Table V., there was a slight increase in the imports of petroleum into the United Kingdom in 1932, although the total was still below the record year of 1930. The total value of these imports was £46,446,831 in 1930, £28,996,606 in 1931, and £21,352,507 in 1933.

TABLE V.

Imports of Petroleum and Its Products into the United Kingdom.

In Imperial gallons.

	1930.	1931.	1932.
Motor spirit ..	954,609,176	905,205,452	974,366,791
Kerosine	245,792,441	270,946,490	220,747,082
Lubricating oil ..	101,937,815	97,531,280	86,605,167
Gas oil	130,822,853	85,041,138	97,717,157
Fuel oil	491,089,111	485,814,062	495,065,001
Crude oil	460,968,094	344,370,004	368,397,387
Other sorts ..	18,532,555	18,318,522	16,431,483
	2,403,752,045	2,207,226,948	2,259,330,068

The *Petroleum Times* has published a series of tables showing the sources of the various products imported into the United Kingdom, and Tables VI. and VII. are extracted therefrom.

TABLE VI.

Imports of Crude Petroleum into the United Kingdom by Countries.

In thousands of Imperial gallons.

Country.	1930.	Per-centage of Total.	1931.	Per-centage of Total.	1932.	Per-centage of Total.
Persia..	338,802	73·5	243,396	70·7	232,294	63·4
Peru	—	—	—	—	45,146	12·2
Dutch West Indies ..	13,291	2·9	23,471	6·8	34,459	9·3
Venezuela	72,322	15·7	70,008	20·4	32,016	8·6
Mexico	—	—	—	—	16,578	4·4
Canary Isles	—	—	—	—	4,524	1·2
United States ..	5,735	1·2	—	—	2,273	0·6
Trinidad	24,480	5·3	7,104	2·1	1,168	0·3
Colombia	6,336	1·4	—	—	—	—
Others	2	—	1	—	—	—
	460,968	100·0	343,980	100·0	368,458	100·0

From Table VI. it will be seen that the sources of the crude petroleum imported for treatment in the United Kingdom have

[1] *Trade Information Bull.* 805, 1932.

undergone some considerable changes. Persia still remains the chief source of supply, although the percentage of the total is lower. Even if all the crude imported from the Dutch West Indies is assumed to have originated from Venezuela, there is still a very large reduction in supplies from that source, and it is to be regretted that the British Empire, as represented by Trinidad, shows a big reduction. The advent of Peru and Mexico in the table are of interest.

TABLE VII.

Imports of Refined Petroleum Products into the United Kingdom by Countries.
In thousands of Imperial gallons.

Country.	1930.	Per-centage of Total.	1931.	Per-centage of Total.	1932.	Per-centage of Total
United States ..	808,620	41·6	575,908	31·0	466,745	24·7
Dutch West Indies	262,603	13·5	336,154	18·0	454,018	24·0
Persia	194,650	10·0	196,272	10·5	260,555	13·7
Rumania	128,463	6·6	199,542	10·7	227,116	12·0
U.S.S.R.	264,462	13·6	268,296	14·4	169,241	9·0
Mexico	149,370	7·7	121,674	6·5	148,375	7·9
Dutch East Indies	43,676	2·3	53,996	2·9	48,030	2·6
Trinidad	49,017	2·5	51,601	2·8	46,035	2·4
Peru	—	—	—	—	27,059	1·4
Straits Settlements and Sarawak ..	25,004	1·3	28,810	1·5	14,021	0·7
Egypt	9,666	0·5	9,589	0·5	13,985	0·7
Others	7,223	0·4	21,922	1·2	17,864	0·9
	1,942,754	100·0	1,863,764	100·0	1,893,044	100·0

Table VII. shows the sources of all refined products imported and it is important to note that the United States shows signs of rapidly losing its position as the principal supplier. As in the case of crude oil, Peru is a newcomer as a source of supply, and several of the other countries show increases in their percentages. Only two decreases of any magnitude are noted, the U.S.S.R. and Straits Settlements and Sarawak.